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Reaction of Lithium-Nitride With Aromatic Aldehydes.

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REACTION OF LITHIUM NITRIDE WITH AROMATIC ALDEHYDES.

The Louisiana State University and Agricultural and Mechanical College, Ph.D., 1969
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REACTION OF LITHIUM NITRIDE WITH AROMATIC ALDEHYDES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

in

The Department of Chemistry

by

Jules M. Morris
B.S., Loyola University of the South, 1959
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August, 1969

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ABSTRACT

Aromatic aldehydes have been shown to react with lithium nitride to yield a complex mixture of compounds resulting from Tischenko (Tischtschenko, Tishchenko), Cannizzaro, benzoin condensation, cyclization, ammonolysis and amidation reactions.

Benzaldehyde reacts vigorously with lithium nitride in refluxing carbon tetrachloride to yield ammonia, benzyl alcohol, benzoic acid salts, benzyl benzoate, benzamide, 2,4,5-triphenylimidazole, threo-N-(2-hydroxy-1,2-diphenylethyl)benzamide and cis-N-(2-benzamido-1,2-diphenylethenyl)benzamide. With p-tolualdehyde, the reaction products include ammonia, p-methylbenzyl alcohol, p-toluic acid salts, p-xylyl p-toluate, p-xylyl p-toluamide, tris-p-tolylimidazole, and cis-N-(2-toluamido-1,2-bis-p-tolylethenyl)-toluamide. Mechanisms are postulated for the formation of these compounds from the respective aldehydes.

Since cis-N-(2-benzamido-1,2-diphenylethenyl)benzamide and cis-N-(2-toluamido-1,2-bis-p-tolylethenyl)toluamide have not been reported previously and since they represent an unusual class of diaryl ethenyl-bis-amides, their chemical and spectral properties were investigated. A summary of the reactions considered include: acid hydrolysis-dehydration; oxidation by potassium dichromate and by elemental bromine in glacial acetic acid; ozonolysis in formic acid; attempted alkaline hydrolysis, pyrolysis and cyclization in refluxing benzoyl chloride or benzoic acid anhydride.

INTRODUCTION

Ionic nitrides, which are among the strongest bases available to organic chemists, have been little studied in the past. Recently, we have become interested in the potential applications of these strong bases in catalyzing organic reactions. Lithium nitride, because of its ready availability (both commercially and laboratory prepared) and ease of handling, was chosen as the most likely representative of the ionic nitrides.

The present investigation resulted from the observation that in addition to catalyzing Cannizzaro and Tischenko reactions with aldehydes containing no α-hydrogens, lithium nitride reacts with aromatic aldehydes to produce a series of complex nitrogen-containing compounds. The express purpose of the present work was to investigate this interesting and complex reaction with a view toward elucidating the nature of the products formed, their mode of formation, and any synthetic utility this reaction may possess.

HISTORICAL

Ionic nitrides are usually prepared by heating the corresponding metal in an atmosphere of nitrogen. Ouvrard,[1] who heated lithium to a dull redness in a stream of nitrogen, was the first to report the preparation of lithium nitride. Lithium also combines slowly with atmospheric nitrogen at room temperature to produce the red or amorphous variety of the nitride. The most convenient laboratory preparation is that described by Masdupy and Gallais[2] in which lithium is heated to 400-500° in an atmosphere of nitrogen. The nitride prepared in this manner is blue-black, highly crystalline and substantially more reactive than that prepared at lower temperatures. Commercial lithium nitride is of the red, less reactive variety. A novel preparation of an ionic nitride, magnesium nitride, was reported recently by Spiers,[3] who heated magnesium ribbon in a tube containing asbestos saturated with concentrated ammonium hydroxide. The gaseous ammonia and steam produced upon heating combine with the magnesium to form both the oxide and the nitride, which are then mechanically separated.

The first report of attempted reaction between organic compounds and ionic nitrides was made by Briegleb and Geuther.[4] They observed that, although phosphorus pentachloride reacted with magnesium nitride to produce magnesium chloride and phosphorus nitride, both absolute alcohol and ethyl iodide were inert, even when heated with magnesium nitride to 160° in a sealed tube. First evidence of reaction came in 1893 when Paschowezky[5] observed a slight reactivity

of magnesium nitride toward phenol, triphenylphosphate, benzyl chloride, and benzoic anhydride. Smits[6] in the same year, reported that urea was reactive toward magnesium nitride while oxalic acid and glycerine appeared to be inert. In 1896, Emmerling[7] reported that at temperatures higher than those used by Briegleb and Geuther, a reaction of absolute alcohol and of ethyl iodide with magnesium nitride was observed. It was also noted that acetic anhydride and benzoic anhydride reacted to produce the corresponding nitriles in 15 and 42% yields respectively. On the other hand, acyl chlorides failed to react. In the following year, Szorvasy[8] reported that methanol reacted with magnesium nitride to give, depending on reaction conditions, either ammonia or trimethylamine; he, however, observed no reaction with ethanol. Snape[9] found chloroform, hexachloroethane, and benzaldehyde quite inert toward magnesium nitride at ordinary temperatures. However, at higher temperatures he reported a vigorous reaction with both chloroform and benzaldehyde. From the reaction with benzaldehyde, he isolated triphenyltriazine (amarone). Orlandi[10] confirmed this observation, but found that benzaldehyde would not react with magnesium nitride in refluxing diglyme. In 1899, Moissan[11] reported the vigorous reaction of ethanol with calcium nitride. Dietrich and Conrad[12] found magnesium nitride useful in water determinations of alcoholic fuels if the volume of methanol was below 60%. They also noted that calcium nitride was totally unsuited for use in these determinations. In the same year, Fichter, Girard, and Erlenmeyer[13] reported that ethanol and butanol reacted with

lithium nitride to yield ammonia and the corresponding alkoxide. Beck,[14] in 1937, reported the formation of lithiumimido and amido acetates by refluxing acetic anhydride in carbon tetrachloride for several days in the presence of lithium nitride.

Relatively recently, Koenig[15] and coworkers became interested in investigating the possible applications of ionic nitrides as catalysts, nucleophiles, and reducing agents in organic reactions.

Although earlier reports[7] stated that acyl chlorides were unreactive toward magnesium nitride, lithium nitride was found to react with aromatic acyl chlorides to give the corresponding tertiary amides. Benzoyl chloride, for instance, reacted with lithium nitride in diglyme to yield tribenzamide as the predominant product. Aliphatic acyl chlorides, on the other hand, were found to give only the corresponding mono- and diamides with none of the tertiary amide being isolated. Compounds containing active hydrogens were found to react in ethereal solvents affording the corresponding organolithium compounds. Fluorene, for example, in refluxing diglyme, produced a deep red solution which, upon carbonation, gave 9-fluorenecarboxylic acid in 31% yield, while the more acidic phenylacetylene in refluxing dioxane gave, after carbonation, phenylpropiolic acid in 72% yield.

Aliphatic aldehydes[15] were found to react very vigorously at 15-20° with catalytic amounts of lithium nitride to give resinous products, along with small amounts of aldols or their dehydration products; crotonaldehyde in 8% yield was obtained from acetaldehyde in this manner. Isobutyraldehyde gave the monoisobutyrate of

2,2,4-trimethyl-1,3-pentanediol in 17% yield upon treatment with lithium nitride at room temperature for three days. Aromatic aldehydes were shown principally to undergo the Tischenko reaction. For instance, benzaldehyde in refluxing carbon tetrachloride reacted rapidly to give benzyl benzoate in 66% yield along with unidentified nitrogen containing side products.

Koenig and Mason[16] sought to investigate the potential uses of lithium nitride as a reducing agent of unsaturated organic substrates. They observed that azobenzene was formed in low yield by the slow reaction of lithium nitride with nitrobenzene in diglyme. Acetone was shown to undergo the aldol condensation with formation of mesityl oxide and isophorone, while aromatic ketones reacted to give the corresponding lithium ketyls and nitrogen. Aromatic nitriles were found to trimerize in the presence of the nitride to yield the corresponding triphenyltriazines as the predominant products. Acetonitrile, on the other hand, reacted in refluxing petroleum ether with the nitride to give 3-iminobutyronitrile and in refluxing diglyme to give 4-amino-2,6-dimethylpyrimidine.

In 1964, Lehn[17] reported the use of lithium nitride in the preparation of substituted silyl and stannyl amines. Tris(trimethylstannyl)- and tris(trimethylsilyl)amines were produced in 59 and 72% yields, respectively, by careful addition of trimethylstannyl chloride and trimethylsilyl chloride to stirred suspensions of the nitride in tetrahydrofuran.

More recently, Koenig and Greene[18] investigated the reaction of lithium nitride with organic esters. They observed that addition of small quantities of the nitride to the refluxing esters produced the corresponding alcohols and amides as the predominant products, with small amounts of diamides and condensation products also being isolated. Ethyl acetate, for instance, gave acetamide (57%), ethanol (100%), and ethyl acetoacetate.

Koenig and Orlandi[10] investigated the reaction of commercially prepared magnesium and calcium nitrides with many of the compounds previously studied with lithium nitride. Quite surprisingly, it was observed that with magnesium nitride, aromatic aldehydes and acyl chlorides gave the corresponding acids, aromatic and aliphatic nitriles were inert, and calcium nitride failed to react with any of the compounds considered.

To date, no other reactions of any significance between ionic nitrides and organic compounds have been reported.

EXPERIMENTAL

Melting points were recorded on a Thomas-Hoover capillary melting point apparatus and were uncorrected. Infrared spectra were determined on a Perkin-Elmer 137B Infracord Spectrometer. Gas chromatographic analyses were performed on a Varian Aerograph Gas Chromatograph, Model A-700. Mass spectral data were determined in this laboratory using a Varian Associates Mass Spectrometer Model M-66. A Varian Associates A-60-A Nuclear Magnetic Resonance (nmr) Spectrometer was used for determining nmr spectra with tetramethyl silane as an internal standard. Elemental analyses were performed in this laboratory by Mr. Ralph Seab and by Galbraith Laboratory, Inc., Knoxville, Tennessee.

Lithium nitride (gratis samples) were supplied by Foote Mineral Co., Exton, Pennsylvania. Reagent grade chemicals and solvents were used as received from commercial sources, except where noted otherwise.

Reaction of Benzaldehyde with Lithium Nitride.

Benzaldehyde (161.2 g., 1.52 mol.) was added over 0.5 hr. to refluxing carbon tetrachloride (690 ml.) containing lithium nitride (12.25 g., 0.248 mol.). Mechanical stirring was applied throughout the following 19-hr. reflux period and a slow stream of dry nitrogen swept any ammonia produced into a hydrochloric acid (1,000 ml., 0.949 N.) trap. Aliquots (1.0 ml.) of the hydrochloric acid were removed at regular intervals and titrated with standard sodium hydroxide solution (0.1022 N.) to a methyl purple endpoint.

Total free ammonia produced in the reaction was 11% (0.031 mol.). The precipitate which formed in the reaction mixture was removed by filtration and washed with additional carbon tetrachloride affording 59.2 g. of dried solid. The reaction filtrate (910 ml. total) was concentrated in vacuo to give the carbon tetrachloride soluble reaction products (125.2 g.).

Reaction Precipitate.

The reaction precipitate (3.84 g.) was extracted with solvents as shown:

Solvent	Volume in ml.	Wt. of Extracted Material in g.	Composition*
Carbon Tetrachloride	100	0.17	Soluble Reaction Products
Acetone	100	1.87	Soluble Reaction Products
Water	2 x 100	1.20	Benzoic Acid Salts
Ethanol	2 x 100	0.00	----------

*Determined by ir.

The insoluble residue remaining after the extractions was identified as crude N-(2-benzamido-1,2-diphenylethenyl)benzamide (Amide I) (0.6 g., 0.0014 mol.), m.p. 270-272°. Recrystallization from DMSO gave pure amide, m.p. 292-294°; ir (Nujol) 3310 cm^{-1} (N-H), 1950, 1900, 1820, 1780 (C_6H_5-), 1650 (C=O); mol. wt. calcd. for $C_{28}H_{22}N_2O_2$, 418.1688; obs. (mass spec.) 418.1587; mass spec. (m/e): 418 (M^+), 400 (M^+-18), 310, 210, 105 ($C_6H_5CO^+$), 89 ($C_6H_5C^+$), 77 ($C_6H_5^+$).

The material obtained in both the carbon tetrachloride and acetone extractions was shown by ir to be identical in composition with the original reaction filtrate. Evaporation of the aqueous extracts gave a white solid which, upon acidification, yielded benzoic acid (1.11 g., 0.0091 mol.) m.p. 120-122° (lit.[19] m.p. 122°); ir (Nujol) 2700 and 2570 cm^{-1} (OH), 1695 (C=O).

The adjusted reaction yields are: the soluble reaction products, 157.6 g.; benzoic acid salts, 18.5 g., (0.140 mol.) in 9.5% yield; N-(2-benzamido-1,2-diphenylethenyl)benzamide, 9.3 g., (0.022 mol.) in 15.5% yield.

Soluble Reaction Products.

Thin layer chromatography (tlc) of the reaction filtrate on Silica Gel-G using cyclohexane and ethyl acetate mixed solvent (90:10) indicated the presence of at least seven components.* Total volatiles in the reaction filtrate were determined by gas chromatography† to be 85%; component compounds were carbon tetrachloride (18.9 g., 12%), benzyl alcohol (17.3 g., 11%), unreacted benzaldehyde (4.7 g., 3%), and benzyl benzoate (94.5 g., 60%). The adjusted reaction yields of benzyl alcohol and benzyl benzoate are 10.8 (0.16 mol.) and 60.6% (0.445 mol.), respectively.

Isolation of *threo*-N-(2-Hydroxy-1,2-diphenylethyl)benzamide (Amide II) and 2,4,5-Triphenylimidazole (TPI).

The reaction filtrate (88.8 g.) was vacuum distilled at 2 mm.

---

*Refer to Appendix A for method and results.
†Refer to Appendix A for conditions.

and four distillate fractions were collected.

Fraction Number	Temperature Range, °C.	Weight (g.)	Composition*
Cold Trap	-------	9.3	Carbon tetrachloride.
1	to 175	18.24	Benzyl alcohol, benzaldehyde, benzonitrile† and benzyl benzoate.
2	175-180	27.74	Benzyl benzoate.
3	180-210	8.6	Benzyl benzoate and threo-N-(2-hydroxy-1,2-diphenylethyl)benzamide.
4	210-250	10.55	Benzyl benzoate and threo-N-(2-hydroxy-1,2-diphenylethyl)benzamide.

*Determined by infrared analysis.
†No direct evidence for the presence of benzonitrile could be found in the original mixture. Its formation has been demonstrated under distillation conditions from the decomposition of hydrobenzamide and N-(2-benzamido-1,2-diphenylethenyl)benzamide.

During collection of the fourth fraction, Amide II solidified in the condenser, and additional amide slowly crystallized from fractions 2 and 3, and especially from fraction 4 upon prolonged standing. Repeated recrystallizations from ethanol gave pure threo-N-(2-hydroxy-1,2-diphenylethyl)benzamide, m.p. 223-224° (lit.[20] m.p. 225°); ir (Nujol) 3310 cm^{-1} (NH), 3220 (weak shoulder H---O=C), 1630 (C=O); nmr (DMSO-d_6) δ 5.05 (broadened t, J_{AB} = 7.0 Hz, J_{AC} = 6.0 Hz, 1 H), 5.35 (broadened t, J_{BA} = 7.0 Hz, J_{BX} = 8.0 Hz, 1 H), ~7.4 (m, 13 H), ~7.6 (m, 2 H), 8.6 (d, J_{BX} = 8.0 Hz, 1 H) (refer to Appendix D, Figure 19); mass spec. (m/e); 212 (M^+-105, C_6H_5CO), 211 (M^+-102, C_6H_5CHO), 194 ([C_6H_5CHOH-$C(C_6H_5)HNH_2$]-18, H_2O), 105 ($C_6H_5CO^+$), 77

($C_6H_5^+$). Additional Amide II (2.5 g., 0.0079 mol.) was isolated from fraction 4 by dilution with methylene chloride. Adjusted yield of threo-N-(2-hydroxy-1,2-diphenylethyl)benzamide (16 g., 0.051 mol.) by ir* estimate is 21% (based on Li_3N).

Anal: Calcd. for $C_{21}H_{19}NO_2$: C, 79.5; H, 6.00; N, 4.42. Found: C, 79.6; H, 5.92; N, 4.28.

The residue from the vacuum distillation was shown by tlc and ir to be 2,4,5-triphenylimidazole† (10 g., 0.034 mol.) in an adjusted yield (17.8 g., 0.0604 mol.) of 48.5% (based on Li_3N). Recrystallization from ethanol gave pure 2,4,5-triphenylimidazole, m.p. 268-272°, (lit.[21] m.p. 274°).

Isolation of Benzamide.

A mixture of fractions 3 and 4 (1.0 g.) was chromatographed over Alcoa Alumina (F-20 grade, 70 g.) with 25 ml. fractions being collected. Benzene eluted fractions 1-15, then benzene-ethanol (90:10) for fractions 16-20, and benzene-ethanol (70:30) for fractions 21-30. Benzamide (< 0.01 g.) was isolated from fractions 21-24, m.p. 123-124° (lit.[20] m.p. 127-127.5°); ir (KBr disc) 3350 and 3170 cm^{-1} (NH), 1660 (C=O), identical with Sadtler[23] spectrum number 2732.

The product yields obtained in the reaction of benzaldehyde with lithium nitride are contained in Table 1.

---

*Refer to Appendix A for method and results.

†Thin layer chromatography data indicate the presence of 2,4,5-triphenylimidazole in the initial reaction mixture; however, some may have arisen from decomposition of dissolved N-(2-benzamido-1,2-diphenylethenyl)benzamide, shown to decompose into 2,4,5-triphenylimidazole under distillation conditions.

TABLE I

REACTION OF BENZALDEHYDE (1.48 mol.) WITH

LITHIUM NITRIDE (0.248 mol.). REACTION YIELDS

Product	Wt. in Grams	Mol.	% Yield Based on Benzaldehyde	% Yield Based on Lithium Nitride
Benzoic Acid	18.5	0.14	9.5	-----
Benzyl Alcohol	17.3	0.16	10.8	-----
Benzyl Benzoate	94.5	0.44	60.8	-----
Amide I	9.3	0.022	6.6	15.5
Amide II	12.3	0.052	3.5	21
TPI	17.8	0.060	12.2	48.5
Benzamide	< 1.0	< 0.008	< 0.5	< 3.2
Ammonia	-----	0.031	-----	11.0

Preparation of Model Compounds of Amide I.

1. Trimer of Benzaldehyde.

The method of preparation of the trimer of benzaldehyde was essentially that of Maimind and Neiman.[24]

A mixture of phenyl azide (10.0 g., 0.084 mol.) and freshly distilled benzaldehyde (200 ml.) was added to refluxing benzaldehyde (600 ml.) over a 2-hr. period. After an additional 0.5-hr. reflux, the excess benzaldehyde was distilled at reduced pressure. The remaining residue was extracted with ether and filtered. Recrystallization from boiling acetic acid gave pure trimer (5.5 g., 0.017 mol.), m.p. 249.8-250.4° (lit.[24] m.p. 245-246°).

Anal. Calcd. for $C_{21}H_{18}O_3$. C, 79.2; H, 5.65.
Found: C, 78.7; H, 5.32.

2. N-(1,2-Diphenylethenyl)Benzamide.

To a stirred suspension of magnesium turnings (8.0 g., 0.33 mol.) in anhydrous ether (100 ml.), was added α-chlorotoluene (46 g., 0.36 mol.) in ether (50 ml.) over 1 hr. under nitrogen. Benzonitrile (20 g., 0.20 mol.) was then added dropwise, followed by ice water. The ether layer containing the crude desoxybenzoinimine was separated and the aqueous layer extracted several times with ether. The combined ether extract was dried over anhydrous calcium chloride and concentrated to 250 ml. To this imine solution, benzoic anhydride (60 g., 0.26 mol.) dissolved in ether (70 ml.) was added over 0.5 hr. After cooling of the mixture, a solid separated. Recrystallization from xylene gave N-(1,2-diphenylethenyl)benzamide (5.7 g., 0.019 mol.)

in 9.5% yield, m.p. 167-169° (lit.[25] m.p. 170°); ir (KBr disc) 3250 cm^{-1} (N-H), 1640 (C=O); nmr (DMSO) δ 6.9 (s, 1 H), ~7.4 (m, 13 H), ~7.9 (m, 2 H), 9.8 (s, 1 H).

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.4; H, 5.68.
Found: C, 83.4; H, 5.68.

3. N-(2-Benzamido-1,2-Diphenylethyl)Benzamide.

Method A - a solution of meso-1,2-diphenylethylenediamine (1.06 g., 4.97 mmol.) in benzene (60 ml.) was slowly added to benzoyl chloride (1.40 g., 9.97 mmol.) dissolved in benzene (50 ml.). The reaction was immediate, as indicated by the formation of a gelatinous precipitate. Filtration was aided by additional benzene (50 ml.). The white solid was washed with ether (200 ml.) and after drying gave N-(2,benzamido-1,2-diphenylethyl)benzamide (2.05 g., 4.87 mmol.) in 98% yield, m.p. > 300° (lit.[20] m.p. > 300°); ir (KBr disc) 3330 cm^{-1} (N-H), 1640 (C=O).

Anal. Calcd. for $C_{28}H_{24}N_2O_2$: C, 80.1, H, 5.72.
Found: C, 79.8; H, 5.87.

Method B - meso-1,2-diphenylethylenediamine (12 g., 0.06 mol.) was added to excess methyl benzoate and the solution was refluxed for 48 hrs. Filtration of the cooled mixture gave pure amide (1.6 g., 0.005 mol.) in 8% yield, m.p. > 300°; ir (KBr disc) 3330 cm^{-1} (N-H), 1640 (C=O), identical to the sample prepared by Method A.

4. cis-N-(2-Benzamidoethenyl)Benzamide.

Excess benzoyl chloride (10 drops) was slowly added to imidazole (0.3 g., 0.04 mol.) dissolved in 10% aqueous sodium hydroxide

(10 ml.). The precipitate was filtered, washed with water, and recrystallized from aqueous ethanol affording cis-N-(2-benzamidoethenyl)-benzamide (0.27 g., 0.014 mol.) in 35% yield, m.p. 204-206° (lit.[26] m.p. 205-206°); ir (nujol) 3300 and 3220 cm^{-1} (NH), 1675 (C=O); mass spec. (m/e): 266 (M^+), 145 (M^+-121, $C_6H_5\overset{O}{\overset{\|}{C}}-NH_2$), 121 ($C_6H_5\overset{O}{\overset{\|}{C}}-NH_2^+$), 105 ($C_6H_5CO^+$), 77 ($C_6H_5^+$); nmr (DMSO-$d_6$) $\delta \sim 6.4$ (m, 2 H), ~ 7.6 (m, 6 H), ~ 7.9 (m, 4 H), 10.1 (d, J = 8 H_2, 2 H).

Anal. Calc. for $C_{14}H_{14}N_1O_1$: C, 72.3; H, 5.26.
Found: C, 71.4; H, 5.31.

5. trans-N-(2-Benzamidoethenyl)Benzamide.

cis-N-(2-Benzamidoethenyl)benzamide (0.1 g., 0.4 mmol.) was heated under a nitrogen atmosphere at 210° for 10 minutes. Recrystallization from 95% ethanol gave the trans isomer (0.05 g., 0.2 mmol.) in 50% yield, m.p. 280-290° (lit.[27] m.p. 280-290°); ir (Nujol) 3310 cm^{-1} (N-H), 1635 (C=O); mass spec. (m/e): 266 (M^+), 145 (M^+-121, $C_6H_5\overset{O}{\overset{\|}{C}}-NH_2$), 121 ($C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2$), 105 ($C_6H_5CO^+$), 77 ($C_6H_5^+$); nmr (DMSO-$d_6$) $\delta \sim 7.3$ (m, 2 H), ~ 7.6 (m, 6 H), ~ 8.0 (m, 4 H), 10.2 (d, J = 8 H_2, 2 H).

Reactions of N-(2-Benzamido-1,2-Diphenylethenyl)Benzamide (Amide I).

Acid Hydrolysis.

Aqueous sulfuric acid (350 ml., 15 M.) and Amide I (6.0 g., 0.014 mol.) were heated under steam distillation conditions. Undissolved amide rapidly disappeared, and steam distillation was continued until 250 ml. of distillate had been collected (ca. 3 hrs.).

The distillate was made basic with sodium carbonate and concentrated. Acidification with hydrochloric acid gave benzoic acid (1.3 g., 0.011 mol.) in 79% yield, m.p. 120-122°; ir (Nujol) 2700 and 2570 cm^{-1} (OH), 1695 (C=O). A mixture melting point with authentic sample gave no depression.

The residue, after cooling, was carefully added to water (850 ml.). This dilution caused the precipitation of crude 2,4,5-triphenyloxazole (4.07 g., 0.0137 mol.) in 98% yield. Recrystallization from ethanol-acetone (99:1) gave pure 2,4,5-diphenyloxazole, m.p. 113-115° (lit.[28] m.p. 114-115.5°). A mixture melting point with an authentic sample prepared by the method of Schonberg[28] gave no depression.

Anal. Calcd. for $C_{21}H_{15}NO$: C, 84.9; H, 5.05. Found: C, 84.2; H, 5.38.

Thermal Decomposition.

Amide I (0.75 g., 1.8 mmol.) was heated at 300° for 15 mins. under a slow stream of dry nitrogen in the apparatus shown in Figure 1. During pyrolysis, a white solid as well as a liquid collected in the ice-water trap. The material (0.25 g.) from the trap was shown by its infrared spectrum to contain benzonitrile, benzoic acid, and benzoic anhydride in an approximate mole ratio of 3:8:1, respectively. The residue remaining after pyrolysis (0.54 g.) was shown by its infrared spectrum to be TPI, essentially free of Amide I. Decolorization with charcoal followed by recrystallization from ethanol-water (200 ml., 1:2) gave 2,4,5-triphenylimidazole (0.4 g., 1.3 mmol.) in 72% yield,

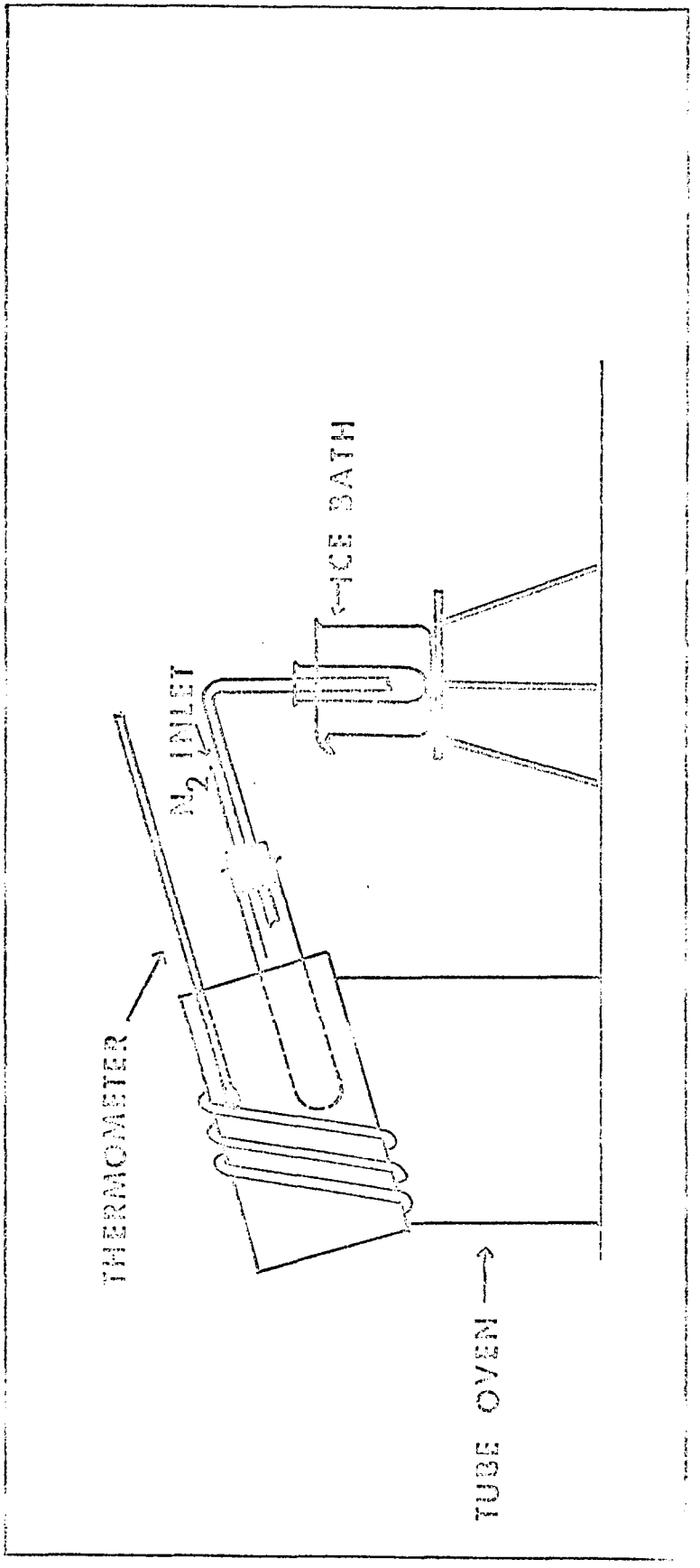

FIGURE 1 Apparatus Used in Pyrolysis Studies

m.p. 273-274° (lit.[21] m.p. 274°); infrared spectrum identical with Sadtler[23] spectrum number 14,151.

Reaction of Amide I with Benzoyl Chloride.

Amide I (1.0 g., 0.0024 mol.) was added to benzoyl chloride (5 ml.) and the mixture refluxed for 0.5 hr. The amide immediately dissolved and remained in solution on cooling. The cooled solution was treated with aqueous sodium hydroxide (10 ml., 20%) and then extracted with ethyl ether (2 x 50 ml.). Evaporation of the ether extracts gave crude 2,4,5-triphenylimidazole (0.4 g., 0.0015 mol.), m.p. 240-260°. Recrystallization from pyridine (10 ml.) by the addition of water (30 ml.) gave pure product (0.35 g., 0.0012 mol.) in 50% yield, m.p. 273-274°, identical in all respects with an authentic sample of TPI.

Reaction of Amide I with Sodium Benzoate and Benzoic Anhydride.

Amide I (0.5 g., 0.0012 mol.) was added to benzoic anhydride (8.0 g., 0.035 mol.) containing sodium benzoate (1.0 g., 0.007 mol.) and the mixture refluxed for 1 hr. The solution was treated with aqueous sodium hydroxide (80 ml., 10%) for 6 hrs. on a steam bath. Filtration, followed by washing of the precipitate with ethanol and water, gave a brown solid (0.42 g.), m.p. 268-272°. Recrystallization from pyridine gave 2,4,5-triphenylimidazole (0.30 g., 0.001 mol.) in 84% yield, m.p. 271-273°.

Similar treatment of the amide with acetic anhydride or propionic anhydride failed to give any indication of reaction.

Ozonolysis of Amide I in Formic Acid.[25]

Amide I (1.0 g., 2.4 mmol.) was dispersed in 97% formic acid (50 ml.). Excess ozone, produced with a Welsbach ozonator, was bubbled through this mixture at room temperature for a total of 6 hrs. Reaction was quite slow and no apparent heat was liberated. After 2 hrs. of ozonation, the amount of unreacted amide remaining dispersed in the formic acid had been reduced and after the third hour most of the amide had dissolved.

The formic acid was removed under reduced pressure, giving 2 g. of residue. This residue was dissolved in petroleum ether (400 ml., b.p. 30-60°) and upon concentrating to 40 ml., benzamide crystallized (0.2 g., 1.6 mmol.) in 33% yield, m.p. 123-5-127°; ir (KBr disc) 3350 and 3170 cm^{-1} (N-H), 1660 (C=O). A mixture melting point with authentic sample gave no depression. Further concentration of the petroleum ether filtrate to 10 ml. gave benzil (0.2 g., 0.001 mol.) in 42% yield, m.p. 94.5-95.5°; ir (KBr disc) 1680 and 1660 cm^{-1} (C=O). A mixture melting point with authentic sample gave no depression. Evaporation of the remaining petroleum ether yielded a yellow solid (0.5 g.). The infrared spectrum of this material indicated the solid to be benzil contaminated with benzamide. Benzamide and benzil were the only two products of ozonolysis isolated.

Oxidation of Amide I with Potassium Dichromate in Glacial Acetic Acid.

To Amide I (1.0 g., 2.4 mmol.) dispersed in glacial acetic acid (100 ml.) was added solid potassium dichromate (1.0 g., 3.4 mmol.)

over a 5-hr. period. The mixture was stirred for an additional 14 hrs. during which time it slowly became a clear green solution. Addition of water (400 ml.) precipitated an unidentified intermediate (0.08 g.), m.p. 200-230°. (This intermediate is converted into the normal end products by treatment with additional potassium dichromate.)

The green filtrate was extracted with ether (2 x 100 ml.). This extract was washed with water (100 ml.), dried over Drierite, filtered, and concentrated to 10 ml. (acetic acid fumes). Addition of water (40 ml.) produced a suspension from which a solid, in the form of long needles, slowly crystallized (0.6 g.), m.p. 130-142°. The infrared spectrum of this material indicated the presence of dibenzamide [ir (KBr disc) 3180 cm^{-1} (N-H), 1695 (C=O)] contaminated with benzil (19%*) [ir (KBr disc) 1680 and 1660 cm^{-1} (C=O)]. Washing of the impure product with ether (100 ml.) gave pure dibenzamide (0.51 g., 2.3 mmol.) in 48% yield, m.p. 146-147° (lit.[29] m.p., 144°); ir (KBr disc) 3180 cm^{-1} (N-H), 1695 and 1665 (C=O). A mixture melting point with authentic dibenzamide produced by the method of Titherly[29] gave no depression.

Oxidation of Amide I with Bromine in Glacial Acetic Acid.

Amide I (1.5 g., 3.5 mmol.) was dispersed in hot glacial acetic acid (50 ml.) and then excess bromine (10 drops) was added. Dissolution was immediate; however, heating on the steam bath was continued for an hour. After cooling, the reaction mixture was concurrently extracted with ether (200 ml.) and water (125 ml.). The

*See Appendix A for method.

ether layer was separated, extracted with a saturated sodium bisulfite solution (2 x 50 ml.) and then washed with water. The aqueous extracts were combined and set aside.

Evaporation of the ether layer gave 0.96 g. of yellow solid, shown by infrared analysis to contain benzamide (29%) and benzil (71%*). This crude reaction product was dissolved in ether (20 ml.) and chilled in a Dry Ice-acetone bath. A small amount of pure benzamide crystallized, m.p. 126-127°; ir (KBr disc) 3350 and 3170 cm^{-1} (N-H), 1660 (C=O). A mixture melting point with authentic benzamide gave no depression. The yellow-green filtrate was evaporated to dryness and a yellow solid (0.85 g.), m.p. 87-88°, was collected. The infrared spectrum of this material indicated the solid to be benzil still contaminated with benzamide. Recrystallization from petroleum ether (b.p. 30-60°) failed to afford pure benzil.

The aqueous extract (from the initial extraction) gave, upon concentrating and acidification, benzoic acid (0.42 g., 3.00 mmol.); identical in all respects to an authentic sample. The benzoic acid resulted from hydrolysis of part of the benzamide† during the bisulfite extraction. Total yields of benzil and benzamide (benzoic acid) formed in the oxidation were 77% (0.58 g., 2.7 mmol.) and 82% (0.70 g., 5.7 mmol.), respectively.

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*See Appendix A for method

†In a separate experiment, it was shown that benzamide hydrolyzed readily in saturated sodium bisulfite solution at room temperature.

Attempted Base Catalyzed Hydrolysis of Amide I.

A mixture containing sodium hydroxide (1.0 g., 25 mmol.), Amide I (1.0 g., 2.4 mmol.), and water (5 ml.) was refluxed for 48 hrs. After cooling of the mixture, only unreacted starting material was isolated.

Other solvents tried were dioxane, diglyme, and diphenyl ether. In each instance, only unhydrolyzed amide was recovered, even after refluxing for several hours.

Model Compounds for Amide II.

N,N'-Benzylidenebisbenzamide.

Benzamide (5.55 g., 0.046 mol.) was heated with benzaldehyde (2.44 g., 0.023 mol.) at reflux until evolution of water stopped (4 hrs.). Upon cooling, the reaction mixture solidified. Recrystallization from ethanol, after charcoal decolorization, gave pure product (7.6 g., 0.023 mol.) in quantitative yield, m.p. 231-232° (lit.[30] m.p. 228°); nmr (DMSO-d_6) $\delta \sim 7.2$ (m, 1 H), ~ 7.5 (m, 11 H), ~ 7.9 (m, 4 H), 8.98 (d, J = 8 Hz, 2 H).

threo-N-(2-Hydroxy-1,2-Diphenylethyl)Benzamide.[31]

To a solution of threo-1,2-diphenyl-2-aminoethanol[20] (0.126 g., 5.94 mmol.) dissolved in benzene (18 ml.) was added benzoyl chloride (0.041 g., 2.93 mmol.) in benzene (1.7 ml.). A white gelatinous precipitate formed immediately and after 15 mins. the reaction mixture was extracted concurrently with chloroform (125 ml.) and water (100 ml.). The chloroform layer, upon evaporation, gave a white solid (0.142 g.). This solid was dissolved in ethanol (70 ml.) and precipitated by the

addition of water (400 ml.) affording pure threo-N-(2-hydroxy-1,2-diphenylethyl)benzamide (0.0688 g., 2.17 mmol.) in 73% yield, m.p. 218-220° (lit.[32] m.p. 223°); ir (Nujol) 3250 cm^{-1} (N-H), 1630 (C=O); nmr (DMSO-d_6) δ 5.05 (broadened t, J_{AB} = 7.0 Hz, J_{AC} = 6.0 Hz, 1 H), 5.35 (broadened t, J_{BA} = 7.0 Hz, J_{BX} = 8.0 Hz, 1 H), ~ 7.4 (m, 13 H), ~ 7.6 (m, 2 H), 8.6 (d, J_{BX} = 8.0 Hz 1 H); mass spec. (m/e): 212 (M^+-105, C_6H_5CO), 211 (M^+-106, C_6H_5CHO), 194 ([C_6H_5-CH(OH)-C(C_6H_5)HNH_2]-18, H_2O), 105 (C_6H_5CO), 77 (C_6H_5).

Reactions of Amide II.

Preparation of threo-N-(2-Benzoyloxy-1,2-Diphenylethyl)Benzamide.

threo-N-(2-Hydroxy-1,2-diphenylethyl)benzamide (0.182 g., 0.57 mmol.) isolated from the reaction of lithium nitride with benzaldehyde was added to excess benzoyl chloride (5 ml.), and the mixture heated for 1 hr. Removal of excess benzoyl chloride by evaporation under nitrogen, produced a solid, which, after washing with benzene (10 ml.) and then cyclohexane (10 ml.), afforded threo-N-(2-benzoyloxy-1,2-diphenylethyl)benzamide (0.240 g., 0.56 mmol.) in 98% yield, m.p. 185-187° (lit.[33] m.p. 187°); ir (Nujol) 3270 cm^{-1} (N-H), 1700 (OC=O), 1640 (NC=O). A mixture melting point with an authentic sample prepared by the method of Soderbaum[31] was undepressed.

Hydrolysis of Amide II.

Amide II (0.0938 g., 0.296 mmol.) was added to refluxing ethanol (25 ml.) containing potassium hydroxide (9.0 g., 0.16 mol.). After 18 hrs., water (70 ml.) was added, followed by extraction with methylene chloride (2 x 50 ml.). The combined methylene chloride

extracts were washed with water (2 x 50 ml.) and evaporated to dryness giving crude threo-1,2-diphenyl-2-aminoethanol (0.0525 g., 0.246 mmol.), m.p. 108-118°, in 83% yield. Recrystallization from chloroform gave pure product (0.0417 g., 0.195 mmol.) in 66.2% yield, m.p. 120-123° (lit.[20] m.p. 125°); ir ($CHCl_3$) 3670 cm^{-1} (OH), 3400 (NH); mass spec. (m/e): 195 (M^+-18, H_2O), 194 (M^+-19), 180 (195-15, NH), 179 (195-16, NH_2), 178 (195-17, NH_3), 166, 106 ($C_6H_5CHO^+$), 79 (C_6H_5-CH_2OH^+), 77 (C_6H_5). A mixture melting point with threo-1,2-diphenyl-2-aminoethanol prepared by the method of Japp and Moir[20] was undepressed.

threo-N-(2-Benzoyloxy-1,2-Diphenylethyl)Benzamide.

threo-1,2-Diphenyl-2-aminoethanol[20] (0.0343 g., 0.16 mmol.) was added to excess benzoyl chloride (5 ml.) and the mixture heated for 1 hr. Removal of excess benzoyl chloride, followed by washing with benzene (10 ml.) and cyclohexane (10 ml.) gave pure threo-N-(2-benzoyloxy-1,2-diphenylethyl)benzamide (0.066 g., 0.156 mmol.) in 97% yield, m.p. 185-187° (lit.[33] m.p. 187°); ir (Nujol) 3270 cm^{-1} (N-H), 1700 (OC=O), 1640 (NC=O).

Reaction of p-Tolualdehyde with Lithium Nitride.

Freshly prepared p-tolualdehyde (8.0 g., 0.066 mol.) was added over 0.5 hr. to refluxing carbon tetrachloride (80 ml.) containing lithium nitride (1.0 g., 0.028 mol.) with mechanical stirring. Following the 10-hr. reflux period and the addition of carbon tetrachloride (100 ml.), the reaction mixture was filtered. Additional precipitate (0.09 g.) slowly formed in the filtrate and necessitated

a second filtration. Concentration of the filtrate under reduced pressure gave soluble reaction product (5.22 g.).

Reaction Precipitate.

The reaction precipitate (4.27 g.) was washed with acetone (50 ml.) and then treated with hot sodium hydroxide solution (50 ml., 20%) for 10 mins. Filtration, followed by acidification of the filtrate with concentrated hydrochloric acid resulted in the formation of a precipitate; filtration and washing with water (200 ml.) gave p-toluic acid (1.4 g., 0.010 mol.), m.p. 175-179°; ir (Nujol) 2670 and 2550 cm^{-1} (OH), 1675 (C=O); nmr ($CDCl_3$) δ 2.45 (s, 3 H), 6.95 (d, J_{AB} = 8 Hz, 2 H), 8.45 (d, J_{BA} = 8 H_z, 2 H), 11.1 (s, 1 H). A mixture melting point with commercial p-toluic acid gave no depression.

The insoluble residue remaining after the sodium hydroxide treatment, as well as that formed in the original filtrate above, was crude N-(2-toluamido-1,2-bis-p-tolylethenyl)toluamide (Amide III) (0.89 g., 0.0019 mol.), m.p. 285-290°. Recrystallization from acetone gave pure Amide III, m.p. 294-296°; ir (Nujol) 3210 cm^{-1} (N-H), 1640 (C=O); mass spec. (m/e): 474 (M^+), 472 (M^+-2), 353 ([M-2]$^+$-119), $CH_3C_6H_5^+$), 339 (M^+-135, $CH_3C_6H_4CONH_2$), 238 (M^{+2}+2), 119, 91.

Anal. Calcd. for $C_{32}H_{30}N_2O_2$: C, 81.0, H, 6.34; N, 5.91. Found: C, 79.4; H, 6.18; N, 5.63.

Soluble Reaction Products.

TLC of the reaction filtrate on Silica Gel G using cyclohexane-benzene-ethanol mixed solvent (65:25:10) indicated the presence of numerous compounds. Partial separation of the mixture into

its components was achieved by chromatographing an aliquot (1.9925 g.) on Silica Gel G (95 g.) with cyclohexane-benzene-ethanol mixed solvent (65:25:10) and collection of 10 ml. fractions. Results are contained in Tables II and III.

Isolation of p-Methylbenzyl Alcohol.

Sublimation of fractions 15-22 at room temperature and atmospheric pressure gave pure p-methylbenzyl alcohol, m.p. 54-58° (lit.[34] m.p. 60°); ir (neat) 3320 and 1035 cm^{-1} (OH), identical with Sadtler[23] spectrum number 9,834; nmr ($CDCl_3$) δ 1.87 (s, 1 H), 2.32 (s, 3 H), 4.60 (s, 2 H), 7.18 (s, 4 H); nmr (CCl_4) δ 2.27 (s, 3 H), 3.47 (broad conc. dependent, 1 H), 4.42 (s, 2 H), 7.05 (s, 4 H). Addition of deuterium oxide resulted in the loss of the singlet at 1.87 δ ($CDCl_3$) and the broad signal at 3.47 δ (CCl_4).

Detection of Unreacted p-Tolualdehyde.

The addition of 2,4-dinitrophenylhydrazine reagent (2 ml.) to fraction 13 (1 ml.) resulted in the formation of an orange-red precipitate. Recrystallization from ethanol gave pure p-tolualdehyde dinitrophenylhydrazone, m.p. 238-240° (lit.[35] m.p. 238-240°).

Isolation of p-Xylyl p-Toluate.

Vacuum distillation of fraction 11 gave p-xylyl p-toluate, b.p. 235-240° (33 mm.) [lit.[36] b.p. 213-217° (15 mm)] in greater than 90% purity; nmr (CCl_4) δ 2.30 (s, 3 H), 2.33 (s, 3 H), 5.19 (s, 2 H), ~ 7.1 (m, 6 H), 7.87 (d, J_{BA} = 8 Hz, 2 H).

TABLE II

REACTION PRODUCTS FROM p-TOLUALDEHYDE (7.74 g., 0.0645 mol.)

AND LITHIUM NITRIDE (1.0 g., 0.028 mol.)

Compound	Wt. in grams	Mol.	% Yield	
			Based on p-Tolualdehyde	Based on Lithium Nitride
p-Toluic Acid	1.472	0.0110	17.0	
p-Methylbenzyl Alcohol	0.280	0.0023	3.6	
Ammonium p-Toluate	0.330	0.0022	3.4	7.9
p-Xylyl p-Toluate	4.230	0.0175	54.5	
N-(2-Toluamido-1,2-bis-p-Tolylethenyl)Toluamide	0.9518	0.0021	13.0	30.0
2,4,5-Tris-p-Tolylimidazole	0.2620	0.0008	3.6	5.7
p-Xylyl p-Toluamide	0.3370	0.0014	4.4	5.0

TABLE III

COLUMN CHROMATOGRAPHY OF p-TOLUALDEHYDE AND LITHIUM NITRIDE REACTION MIXTURE

Fraction No.	Description	Wt. of Fract., Grams	COMPOSITION IN GRAMS							
			Aldehyde	Alcohol	Ester	Amide III	TTI	Amide VI	p-Toluic Acid	Ammonium p-Toluate
1-9	CCl_4 soluble	0.0111								
10	CCl_4 soluble	0.0555								
11	CCl_4 soluble	0.6226			0.6226[a]					
12	Small amt. of Precipitate	0.4788	0.0288[a]		0.4500[a]	Small amt.				
13	Small amt. of Precipitate	0.1880	0.0466[a]		0.0406[a]	0.0236[b]	0.0772[a]			
14	Small amt. of Precipitate	0.0717	0.0288[a]	0.0030[a]		Small[b] Amt.	0.0228	Small Amt.		
15-22	Small amt. of Precipitate	0.2590	0.0026[a]	0.1585[a]			Small[b] Amt.	0.0950[b]		
23-30	Small amt. of Precipitate	0.0150						0.0150[b]		
31-40	Small amt. of Precipitate	0.0184						0.0184[b]		
41-54	Small amt. of Precipitate	0.0013							0.0013[c]	
55-74	Small amt. of Precipitate	0.0115							0.0115[c]	
76-94		0.0049							0.0049[c]	
95-111		0.0096							0.0096[c]	
112-215										
216-240[d]		0.1096								0.1096
241-250[d]		0.0174								0.0174
	TOTALS	1.8744	0.1068	0.1615	1.1132	0.0236	0.1000	0.1284	0.0275	0.1270

a. NMR data. b. IR data.
c. TLC data. d. Solvent - 95% ethanol.

Isolation of p-Xylyl p-Toluamide (Amide VI) and 2,4,5-Tris-p-Tolylimidazole (TTI).

A part of the initial reaction filtrate was distilled (1.5 mm.) with collection of two distillate fractions: fraction 1 from ambient temperature to 175°, and 2 from 175-225°. Both fractions were shown by nmr to consist mainly of p-xylyl p-toluate; however, during collection of the second fraction, p-xylyl p-toluamide solidified in the condenser and also slowly crystallized in fraction 2. Repeated recrystallizations from ethanol gave pure Amide VI, m.p. 164-166°; ir (Nujol) 3300 cm^{-1} (N-H), 1640 (C=O); nmr (DMSO-d_6) δ 2.29 (s, 3 H), 2.37 (s, 3 H), 4.46 (d, J_{AX} = 6 Hz, 2 H), 7.0 (d, J_{AB} = 8 Hz, 2 H), 7.16 (s, 4 H), 8.1 (d, J_{BA} = 8 Hz, 2 H), 8.82 (broad, 1 H). Addition of deuterium oxide caused slow collapse of the doublet at δ 4.46 to a singlet and slow loss of N-H signal at δ 8.82. Pure Amide VI was also obtained from fractions 15-40 collected by column chromatography.

The distillation residue was shown by tlc to be mainly 2,4,5-tris-p-tolylimidazole. Recrystallization from ethanol-water (2:1) gave pure TTI, m.p. 232-233° (lit.[37] m.p. 234°); nmr ($CDCl_3$) δ 2.38 (broad singlet, 9 H), 7-8 (m, 12 H).

Reactions of N-(2-Toluamido-1,2-bis-p-Tolylethenyl)Toluamide (Amide III).

Acid Hydrolysis of Amide III.

Aqueous sulfuric acid (25 ml., 15 M.) and Amide III (0.054 g., 1.1 mmol.) were heated under steam distillation conditions for 3 hrs. Undissolved amide rapidly dissolved and p-toluic acid, m.p. 177-170°;

infrared spectrum identical with Sadtler[23] spectrum number 2152, was collected in the distillate. The residue, after cooling, was carefully added to water (100 ml.). This dilution caused precipitation of 2,4,5-tris-p-tolyloxazole, (0.024 g., 1.0 mmol.) in 91% yield. Recrystallization from absolute ethanol gave pure product, m.p. 143-145° (lit.[28] m.p., 145°).

Pyrolysis of Amide III.

Amide III (0.2 g., 0.43 mmol.) was heated for 10 mins. at 300° under a slow stream of dry nitrogen in the apparatus shown in Figure 1. The distillate (0.02 g.) was shown by its infrared spectrum to contain p-tolunitrile, p-toluic acid, and p-toluic anhydride. The residue remaining after pyrolysis was extracted with ethanol (25 ml.), filtered, decolorized with charcoal and recrystallized to give 2,4,5-tris-p-tolylimidazole (0.13 g., 0.38 mmol.) in 90% yield, m.p. 232-233° (lit.[37] m.p. 234°); nmr ($CDCl_3$) δ 2.38 (broad singlet, 9 H), 7-8 (m, 12 H).

Preparation of p-Tolualdehyde by Formylation of Toluene.

Hydrogen chloride and carbon monoxide were passed for 4 hrs. through a mixture containing dry toluene (200 g., 2.17 mol.), freshly-prepared cuprous chloride (30 g., 0.15 mol.), and anhydrous aluminum chloride (300 g., 2.2 mol.).

The reaction mixture was hydrolyzed by pouring over ice (1500 g.). The organic layer was separated and distilled giving p-tolualdehyde (30 g., 0.25 mol.) in 11% yield, b.p. 199-201° (lit.[38] b.p. 203-205°).

The nmr spectrum indicated the presence of the isomeric o-tolualdehyde (12.5%) in the product; as determined by CH_3 integration, δ 2.42 (p-CH_3), 2.61 (o-CH_3).

Alternate Preparation of p-Tolualdehyde.

1. Preparation of p-Toluanilide.[39]

A mixture of p-toluic acid (100 g., 0.74 mol.) and aniline (69 g., 0.74 mol.) was heated at 180° for 3 hrs. The temperature was then gradually increased to 225° and held for 2 hrs. Excess aniline 50 g., 0.54 mol.) was added and the heating cycle repeated. Total water (8.3 ml.) collected in the distillate indicated a 62% yield of p-toluanilide. The crude p-toluanilide separated when the reaction mixture was cooled. Washing the filtered crude product with 1 N hydrochloric acid (2 x 50 ml.), 1 N sodium hydroxide (2 x 50 ml.) and finally water, gave pure product (93 g., 0.44 mol.) in 60% yield, m.p. 145.5-147° (lit.[40] m.p. 145-146°).

2. Preparation of N-Phenyl-p-Toluimidyl Chloride.[41]

p-Toluanilide (93 g., 0.44 mol.) in dry benzene (100 ml.) was treated cautiously with phosphorus pentachloride (150 g., 0.70 mol.). The mixture was heated at 75° for 15 mins. and then distilled under reduced pressure to remove most of the phosphorusoxychloride yielding crude N-phenyl-p-toluimidyl chloride.

3. Reduction of N-Phenyl-p-Toluimidyl Chloride.

Dry hydrogen chloride was bubbled through a mixture of anhydrous stannous chloride (250 g., 1.3 mol.) and dry ether (1125 ml.) until a clear bottom phase formed (2 hrs.). The crude N-phenyl-p-

toluimidyl chloride (from Part 2) was then carefully added. The mixture was stirred for 1 hr., followed by standing at room temperature for 8 hrs. Ice (400 g.) was added and the ether was removed by distillation. Crude p-tolualdehyde was then collected by steam distillation. Separation of the p-tolualdehyde followed by calcium chloride drying and distillation gave pure aldehyde (10 g., 0.083 mol.) in 19% yield, b.p. 199-201° (lit.[38] b.p. 203-205°); nmr (CCl_4) δ 2.42 (s, 3 H), 7.00 (d, J_{AB} = 8 Hz, 2 H), 7.90 (d, J_{BA} = 8 Hz, 2 H), 9.94 (s, 1 H).

Preparation of meso-1,2-Diphenylethylenediamine.[42]

1. Preparation of erythro-N-(2-Benzylideneamino-1,2-Diphenylethyl)Benzamide.[43]

Benzaldehyde (420 g., 4.0 mol.) and ammonium acetate (160 g., 2.1 mol.) were refluxed for 3 hrs. The refluxing solution gradually turned bright yellow and product precipitated. The solid was collected by filtration and washed with ethanol until colorless to give pure amide (165 g., 0.42 mol.) in 42% yield, m.p. 256-259° (lit.[42] m.p. 259°). Recrystallization was unnecessary prior to hydrolysis (see below).

2. Hydrolysis of erythro-N-(2-Benzylideneamino-1,2-Diphenylethyl)Benzamide.

A mixture of erythro-N-(2-benzylideneamino-1,2-diphenylethyl-benzamide (50 g., 0.13 mol.), water (500 ml.) and concentrated sulfuric acid (270 ml.) was steam distilled until benzoic acid no longer appeared in the distillate (6-10 hrs.). The cooled sulfuric acid

solution was carefully neutralized with ammonium hydroxide (7 M., 1200 ml.). Solid meso-1,2-diphenylethylenediamine precipitated upon neutralization and was collected by filtration. Recrystallization from petroleum ether (b.p. 30-60°) containing acetone (5%) gave the pure diamine (23 g., 0.11 mol.) in 83% yield, m.p. 118-119.5° (lit.[44] m.p. 119.5°); mass spec. (m/e): 195 (M^+-17), 194, 193, 180 (M^+-32), 179, 178 (M^+-34), 165, 106 ($C_6H_5CHNH_2^+$), 91 ($C_6H_5CH_2^+$), 89 ($C_6H_5C^+$), 51.

Preparation of threo-1,2-Diphenyl-2-Aminoethanol.[20]

To meso-1,2-diphenylethylenediamine (1.1 g., 5.2 mmol.) dissolved in sulfuric acid (30 ml., 4 M.) was added solid sodium nitrite (0.75 g., 0.011 mol.). The reaction mixture was heated on the steam bath for 5 mins., cooled, and neutralized by careful addition of concentrated ammonium hydroxide. Extraction of the mixture with benzene (2 x 25 ml.), followed by filtration and concentration to 20 ml. gave the slightly yellow threo-1,2-diphenyl-2-aminoethanol (0.2 g., 0.94 mmol.) in 18% yield, m.p. 118-123° (lit.[20] m.p. 125°).

Preparation of erythro-1,2-Diphenyl-2-Aminoethanol.

Method A[45] - Benzoin oxime (1.85 g., 9.5 mmol.) was mixed with aqueous sodium hydroxide solution (28 ml., 10%) on a steam bath and zinc dust (4.2 g., 0.065 mol.) was added in 4 increments over a 3-hr. period. The cooled mixture was acidified with hydrochloric acid (6 N). Extraction with methylene chloride, followed by concentration of the extract yielded a small amount of white solid. Thin-layer chromatography indicated the presence of numerous compounds; therefore, this method was abandoned.

Method B - Benzoin oxime (5 g., 0.02 mol.) was stirred in 95% ethanol (70 ml.) for 0.5 hr., while sodium amalgam (71.5 g., 2.4% sodium) and glacial acetic acid (15 ml.) were added in proportionate amounts. Addition of water (200 ml.) and ammonium hydroxide produced a hazing of the mixture. Extraction with methylene chloride (2 x 100 ml.) yielded 2.0 g. of crude product, which was purified chromatographically on Alcoa Alumina (F-20 grade, 40 g.) eluting with benzene; then benzene-ethanol (90:10), (85:15), and (75:25) solvent mixtures with collection of 40 ml. fractions. Fractions 15-21 were concentrated to give erythro-1,2-diphenyl-2-aminoethanol (1 g., 4 mmol.) in 20% yield, m.p. 161-162° (lit.[46] m.p., 161°); mass spec. (m/e): 195 (M^+-18), 194 (M^+-19), 180 (M^+-33, OH, NH_2), 179, 178, 166, 152, 106 ($C_6H_5CHO^+$), 79 ($C_6H_5^+$), 77 ($C_6H_5^+$).

Preparation of Dibenzamide.

Benzoyl chloride (14 g., 0.1 mol.) was added over 15 mins. to a solution of benzamide (12 g., 0.1 mol.) in pyridine (60 ml.), cooled in an ice-water bath. After 8 hrs., the reaction mixture was shaken with water (240 ml.). The resulting organic layer was extracted concurrently with ether (500 ml.) and 3 N sulfuric acid. The dried ether layer, upon concentration, gave pure dibenzamide (2 g., 0.01 mol.) in 10% yield, m.p. 146-149° (lit.[29] m.p. 148-150°); ir (KBr disc) 3180 cm^{-1} (N-H), 1695 and 1665 (C=O).

Preparation of 2,4,5-Triphenylimidazole.

A mixture containing benzil (52.5 g., 0.25 mol.), ammonium acetate (250 g., 3.2 mol.) and glacial acetic acid (1250 ml.) was

refluxed for 1 hr. Addition of water (1 l.) to the cooled reaction mixture precipitated unreacted benzil (33 g., 0.16 mol.), m.p. 88-90°. Further dilution to a total volume of 10 l. gave crude product (20.0 g., 0.068 mol.), m.p. 200-240°. Recrystallization from pyridine-water (3:1) gave pure 2,4,5-triphenylimidazole (4.7 g., 0.016 mol.), m.p. 273.5-274.5° (lit.[21] m.p. 274°). A second crop (17.9 g., 0.061 mol.), m.p. 270-273°, was obtained by addition of excess water to the above filtrate, for a total yield of 46%; infrared spectrum identical with Sadtler[23] spectrum number 14,151.

Preparation of 2,4,5-Triphenyloxazole.

Benzil (10 g., 0.048 mol.) and aqueous ammonia (25 ml.) were heated in a pressure vessel for 6 hrs. at 120-130°. The tacky reaction residue was recrystallized from ethanol (100 cc.) containing acetone (1%) to give 2,4,5-triphenyloxazole (2.0 g., 0.0067 mol.) in 28% yield, m.p. 113.5-115° (lit.[28] m.p. 114-115.5°); infrared spectrum identical with Sadtler[23] spectrum number 14,103.

Anal. Calcd. for $C_{21}H_{15}NO$: C, 84.8; H, 5.05
Found: C, 84.2; H, 5.38.

Preparation of Hydrobenzamide.

Gaseous ammonia was slowly bubbled through precooled (-80°) benzaldehyde (106 g., 1.0 mol.) for several hours. The crude hydrobenzamide was filtered and pressed dry. Recrystallization from cyclohexane, followed by washing with cyclohexane (50 ml.) and ethanol (50 ml.) yielded product, m.p. 96-105°. A second recrystallization from cyclohexane yielded pure hydrobenzamide (11.9 g., 0.04 mol.) in

12% yield, m.p. 102-103° (lit.[47] m.p. 101°); ir (KBr disc) 2810 cm^{-1} (C-H), 1650 (C=N), identical with Sadtler[23] spectrum number 20,378; nmr (CCl_4) δ 5.80 (s, 1 H), ~7.2 (m, 11 H), ~7.6 (m, 4 H), 8.33 (s, 2 H).

Preparation of Benzoin Oxime.

A mixture containing benzoin (20 g., 0.095 mol.), ethanol (50 ml.), hydroxylamine hydrochloride (18 g., 0.26 mol.), sodium hydroxide (8.8 g., 0.22 mole), and water (70 ml.) was refluxed for 4 hrs. Water (300 ml.) was added to the hot solution; unreacted benzoin precipitated and was removed by filtration. Benzoin oxime slowly crystallized from the cooled filtrate. Recrystallization from aqueous ethanol gave pure oxime (10.5 g., 0.046 mol.) in 48% yield, m.p. 150-151°; infrared spectrum identical with Sadtler[23] spectrum number 2,718.

Reaction of Benzaldehyde with Gaseous Ammonia.

A solution containing benzaldehyde (25.0 g., 0.234 mol.) and carbon tetrachloride (200 ml.) was refluxed for 8 hrs. while gaseous ammonia was bubbled through the solution. The carbon tetrachloride was removed under reduced pressure, and crystals of hydrobenzamide [(6.8 g., 0.023 mol.), m.p. 102-104° (lit.[47] m.p., 101°), ir (KBr disc) 2810 cm^{-1} (C-H), 1650 (C=N)] slowly formed in the reaction residue. The total yield of hydrobenzamide was estimated to be 56% (6.2 g.). (This estimate was based on the experimentally determined solubility of hydrobenzamide in benzaldehyde and on an infrared spectrum comparison.)

Acid Hydrolysis of N-(1,2-Diphenylethenyl)Benzamide.

A mixture of aqueous sulfuric acid (90 ml., 6 M) and N-(1,2-diphenylethenyl)benzamide (1.2 g., 4 mmol.) was steam distilled until solid no longer appeared in the distillate (ca. 8 hrs.). Impure desoxybenzoin (0.5 g., 2.5 mmol.) was recovered by filtration of the distillate in 62% yield; infrared spectrum identical with Sadtler[23] spectrum number 7197. The filtrate was made basic with sodium carbonate and concentrated to 25 ml. Addition of sulfuric acid (10 ml., 6 M) gave benzoic acid (0.4 g., 3 mmol.) in 75% yield; ir (Nujol) 2700 and 2570 cm^{-1} (OH), 1695 (C=O), identical with Sadtler[23] spectrum number 14,151.

Acid Hydrolysis of Benzamide.

A mixture of aqueous sulfuric acid (90 ml., 6 M.) and benzamide (5.35 g., 0.044 mol.) was heated under steam distillation conditions until benzoic acid no longer appeared in the distillate. The distillate was made alkaline with sodium carbonate, concentrated to 10 ml. and slowly acidified with 6 M hydrochloric acid. The crude benzoic acid was collected by filtration, washed with water (100 ml.) and dried to give pure benzoic acid (5.3 g., 0.044 mol.) in quantitative yield, m.p. 120-122°.

Attempted Pyrolysis of 2,4,5-Triphenylimidazole (TPI).

TPI (0.22 g., 0.74 mmol.) was heated at 285° for 0.5 hr. under a slow stream of dry nitrogen in the apparatus shown in Figure 1. No distillate collected in the ice-water trap, although sublimation had taken place on the walls of the test tube. The infrared spectrum

of both the sublimate and residue were identical to that of the starting material.

Attempted Pyrolysis of 2,4,5-Triphenyloxazole.

2,4,5-Triphenyloxazole (0.5 g., 1.7 mmol.) was heated at 300° for 1 hr. under a slow stream of dry nitrogen in the apparatus shown in Figure 1. The infrared spectrum of both the distillate and residue indicated the presence of only undecomposed starting material.

Pyrolysis of Hydrobenzamide.

Hydrobenzamide (1.06 g., 3.5 mmol.) was heated at 270° for 0.5 hr. under a slow stream of dry nitrogen in the apparatus shown in Figure 1. The liquid which collected in the ice-water trap was shown by its infrared spectrum to be a mixture of toluene and benzonitrile, while the residue consisted entirely of TPI.

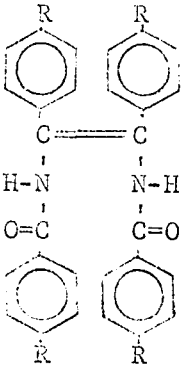
Distillation and Pyrolysis of Hydrobenzamide.

Hydrobenzamide (5.0 g., 0.017 mol.) was distilled at 1 mm., and two distillate fractions (1.2 g. total) were collected over the range 225-250°; both were essentially pure hydrobenzamide. The infrared analysis of both fractions failed to indicate the presence of benzonitrile (formed in atmospheric pyrolysis of hydrobenzamide). The distillation residue was shown by its infrared spectrum to be 2,4,5-triphenylimidazole (3.8 g., 0.013 mol.) with no residual hydrobenzamide detectable.

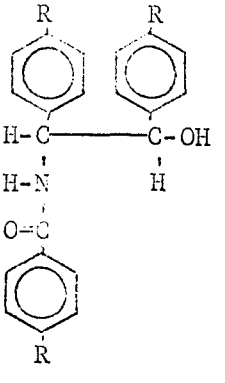
RESULTS AND DISCUSSION

Reaction of Aromatic Aldehydes with Lithium Nitride.

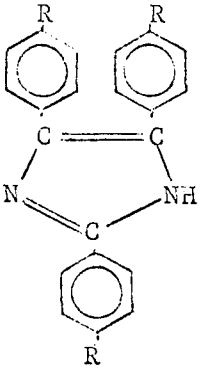
Lithium nitride has been observed to react vigorously after short induction periods with aromatic aldehydes dissolved in refluxing carbon tetrachloride solution. The reaction, which at least initially proceeds on the surface of the insoluble nitride, is complex in character as evidenced by the formation of a variety of seemingly unrelated products. For example, with benzaldehyde, ammonia, benzyl benzoate, benzyl alcohol, benzoic acid salts, cis-N-(2-benzamido-1,2-diphenylethenyl)benzamide(I), threo-N-(2-hydroxy-1,2-diphenylethyl)benzamide(II), 2,4,5-triphenylimidazole(IV), and benzamide have been isolated. With p-tolualdehyde, the reaction products include: ammonia, p-xylyl p-toluate, p-methylbenzyl alcohol, ammonium p-toluate, cis-N-(2-toluamido-1,2-bis-p-tolylethenyl)toluamide(III), 2,4,5-tris-p-tolylimidazole(V), and p-xylyl p-tolamide.



I, R = H
III, R = CH_3



II



IV, R = H
V, R = CH_3

Clearly, the reaction proceeds by at least several different, independent mechanisms. Firstly, the condensation products, which are normally anticipated in the base catalyzed reactions of aromatic aldehydes, are discussed in terms of Cannizzaro and/or Tischenko reaction mechanisms. Secondly, the complex nitrogen-containing products are considered as resulting from base catalyzed benzoin condensations followed by various addition, elimination, and cyclization reactions.

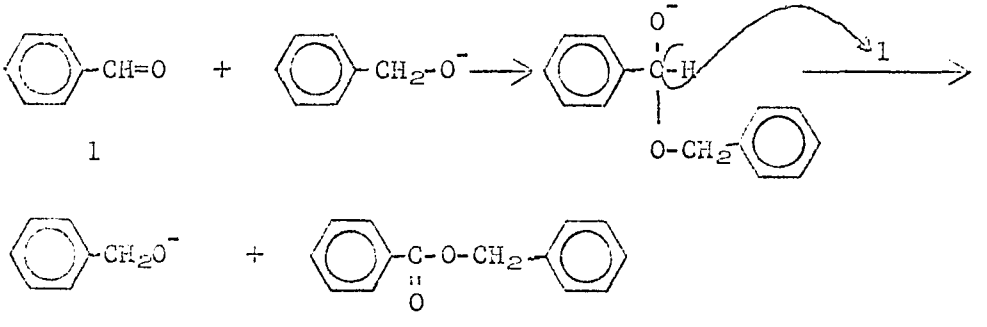
As a result of the complex nature of these reactions and the difficulty encountered in the isolation and characterization of the products formed, no attempt has been made to test the postulated mechanisms.

Ester Formation.

In the reaction of benzaldehyde and p-tolualdehyde respectively, with lithium nitride, the corresponding esters are isolated in 60.6 and 54.5% yields, respectively, as the predominant products. This self-condensation of aldehydes which do not contain α hydrogens, known as the Tischenko reaction, can be catalyzed by a variety of substances. Claisen,[48] in 1887, while studying the Cannizzaro reaction of benzaldehyde, noted the formation of substantial amounts of benzyl benzoate (40%) when sodium methoxide was employed as catalyst. Tischenko,[49] employing aluminum ethoxide as catalyst, developed the method into a useful synthetic route to esters and extended the scope of this reaction to include the formation of aliphatic, as well as aromatic esters from the corresponding aldehydes, benzyl benzoate being produced in 88% yield from benzaldehyde with this catalyst.

Sodium benzylate[50] and sodium hydride[51] have also been successfully utilized in effecting high yields of esters, benzyl benzoate being formed from benzaldehyde in 92 and 85% yields, respectively. Organometallics (t-butyllithium and n-butylmagnesium chloride[52]) as well as complex catalyst systems [ethyl acetate (83%), ethanol (11.7%), aluminum (2.8%), aluminum chloride (1.5%), ferric chloride (0.5%) and water (0.45%)[53]] have been used to advantage in promoting Tischenko reactions. There has also been at least one report of a Tischenko reaction occurring in the absence of catalyst. Finch[54] in 1960, noted the formation of 3-hydroxy-2,2-dimethylpropyl-3-hydroxy-2,2-dimethyl propionate [$HO\text{-}CH_2\text{-}C(CH_3)_2\text{-}CO_2\text{-}CH_2C(CH_3)_2CH_2OH$] in 93% yield by heating hydroxypivaldehyde in the absence of any added catalysts.

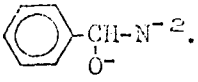
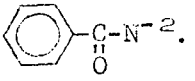
The formation of esters from the corresponding aldehydes has long been recognized to be an ionic chain reaction requiring only small amounts of catalysts. The formation of benzyl benzoate by the addition of sodium benzylate to benzaldehyde, for example, involves nucleophilic attack by the benzylate ion on the aldehyde followed by intermolecular hydride ion shift with subsequent formation of ester and regeneration of benzylate ion[55] with only catalytic amounts of benzylate ion necessary.



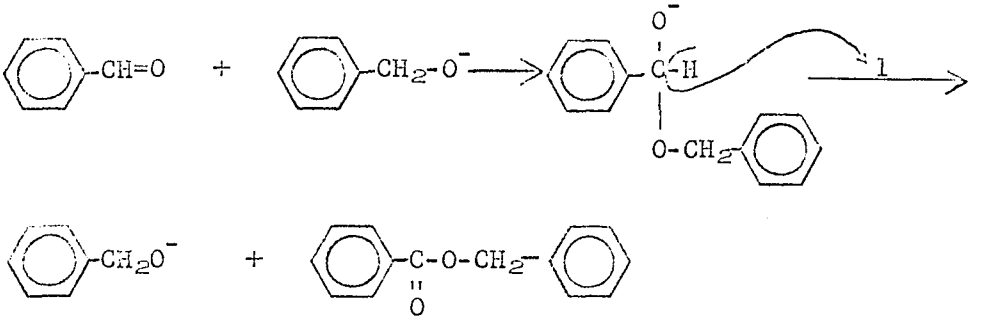
Essentially the same mechanism had been proposed earlier by Swamer and Hauser[56] for the formation of the ester from benzaldehyde and sodium hydride. They postulated the formation of trace amounts of sodium benzylate by direct reduction of benzaldehyde with the hydride, which then catalyzed the observed Tischenko reaction. In 1965, Lewis[55] reported somewhat different results for the reaction of p-nitrobenzaldehyde with sodium hydride and although some ester was isolated, most of the aldehyde was consumed via the Cannizzaro mechanism. He attributed this observed difference in reaction paths to oxygen containing nucleophiles present on the surface of the hydride (formed by reaction of the hydride with atmospheric oxygen and moisture). Although no analytical data were available to support this contention, he observed that both sodium hydroxide and sodium peroxide effected the Cannizzaro reaction under similar conditions. He also noted that sodium hydride from containers that had been opened extensively gave higher yields of Cannizzaro products than did fresh hydride. He concluded that the contribution of the hydride in the reaction is to provide a large surface area for the absorption of oxygen, conversion of this oxygen to oxygenated nucleophiles, and absorption of organic reactants.

In the formation of ester by the reaction of benzaldehyde and p-tolualdehyde with lithium nitride, several mechanistic schemes thus appear plausible.

Firstly, absorption of aldehyde on the nitride surface would be followed by nucleophilic attack by the immobile nitride ion on the

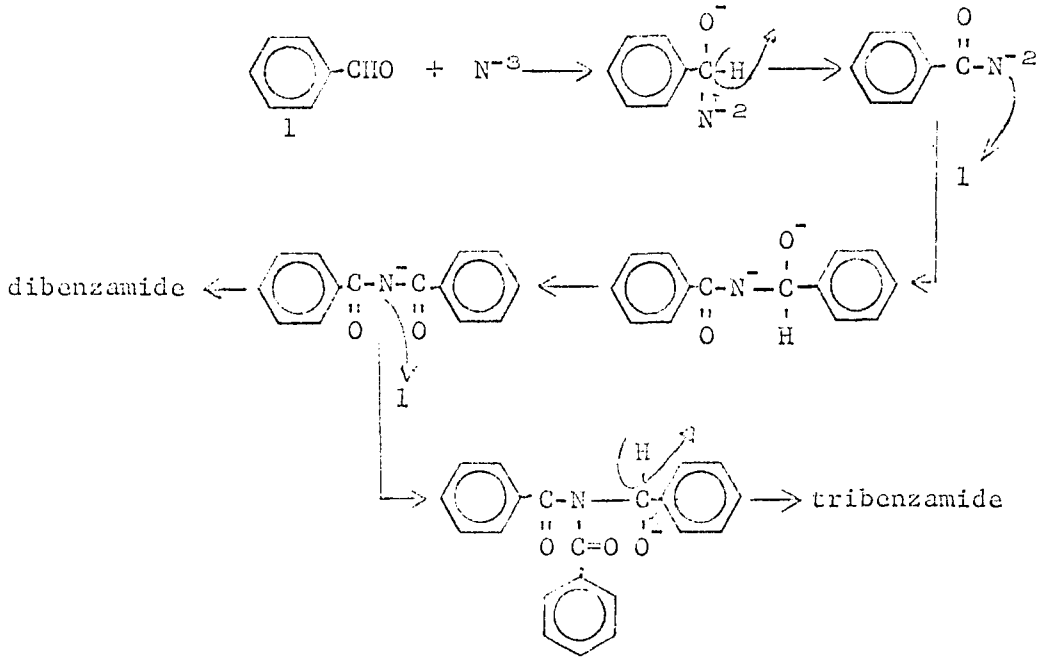
carbonyl carbon with the formation of  . The formation of this species could be rationalized on the basis of delocalization of a portion of the high negative charge of the nitride ion on the more electronegative oxygen atom. Further stabilization of this species could occur by loss of a hydride ion with the formation of the corresponding imido ion  . The freed hydride ion, as proposed by Swamer and Hauser[51] above, would react with benzaldehyde to produce the benzylate ion which could then catalyze the formation of ester.

In the second scheme, oxygen-containing impurities absorbed on the surface of the nitride, and formed there by the action of atmospheric oxygen and moisture, would react with the absorbed aldehyde to produce trace quantities of benzyl alcohol and lithium benzoate via the Cannizzaro mechanism.[55] The benzyl alcohol would then be converted to lithium benzylate by reaction with nitride, thereby activating the Tischenko mechanism.



Although no direct evidence is available to favor one mechanism over the other, the second is preferred because both steps (Cannizzaro reaction catalyzed by oxygen-containing surface impurities and reaction of ionic nitrides with alcohols) are described in the

literature. Also, if initial reaction of aldehyde with lithium nitride involved the elimination of hydride ion, subsequent formation of dibenzamide and tribenzamide would be anticipated as follows:



Neither dibenzamide nor tribenzamide could be isolated from the reaction mixture.

Alcohol and Acid Formation.

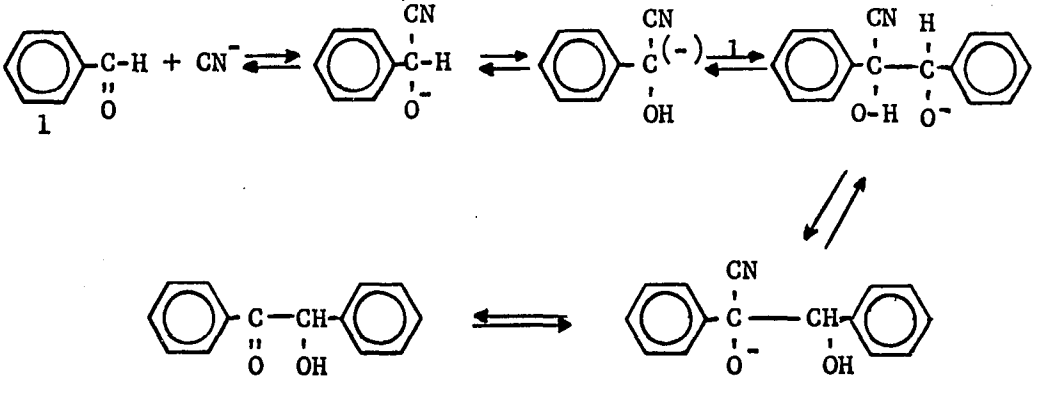
In the reaction of aromatic aldehydes with lithium nitride, Cannizzaro products are formed in substantial amounts. Benzaldehyde, for example, afforded benzyl alcohol and benzoic acid in 10.8 and 9.8% yields, while p-tolualdehyde gave p-methylbenzyl alcohol and p-toluic acid in 3.6 and 17.0% yields, respectively.

The isolation of the alcohols as such from the reaction mixture indicates a delayed formation after all the lithium nitride has been consumed or poisoned. Slow hydrolysis of the corresponding ester

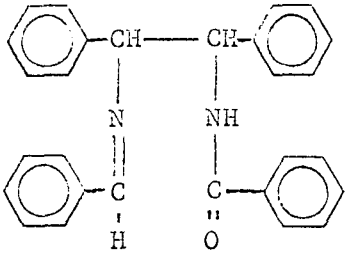
by lithium hydroxide (formed from lithium nitride and water, which is produced in reactions to be discussed later) could yield the alcohol and acid salts observed. This slow organic phase hydrolysis has been proposed[56] as one of the mechanisms by which heterogeneous Cannizzaro reactions proceed. The expected molar ratio of acid to alcohol (1:1) is obtained with benzaldehyde (within experimental error), while the much higher ratio observed with p-tolualdehyde could result from autoxidation of the alcohol or aldehyde to the acid.[55]

Benzoin Condensation of Aromatic Aldehydes.

The reaction of aromatic aldehydes with the formation of the corresponding benzoins is usually effected in alcoholic solution by alkali metal cyanides. The mechanism generally accepted for this reaction[57] involves the addition of cyanide ion to the carbonyl carbon of the aldehyde, followed by condensation of the resulting anion with another molecule of the aldehyde. Hydrogen ion migration and elimination of cyanide ion yields the corresponding benzoin.



Catalysts other than alkali metal cyanides have been used in effecting benzoin type condensations. Magnesium metal plus a crystal of iodine,[58] for example, converts refluxing benzaldehyde into benzoin in 40% yield, while benzaldehyde is reported to form various products via benzoin condensation upon treatment with ammonium amalgam.[59] Benzoin has also been produced in 50% yield by Kharasch[60] upon treatment of ethyl benzoate with sodium dissolved in liquid ammonia. The most pertinent example of a benzoin condensation was reported by Trippet[43] in 1957. He repeated the work of Pinner[61] in which benzaldehyde was refluxed with ammonium acetate and identified the product, which crystallized upon cooling of the mixture, as erythro-(2-benzylideneamino-1,2-diphenylethyl)benzamide:



obviously, the product of a benzoin condensation. Although a mechanism was not postulated to support this contention, he noted that under similar conditions, p-tolualdehyde failed to react.

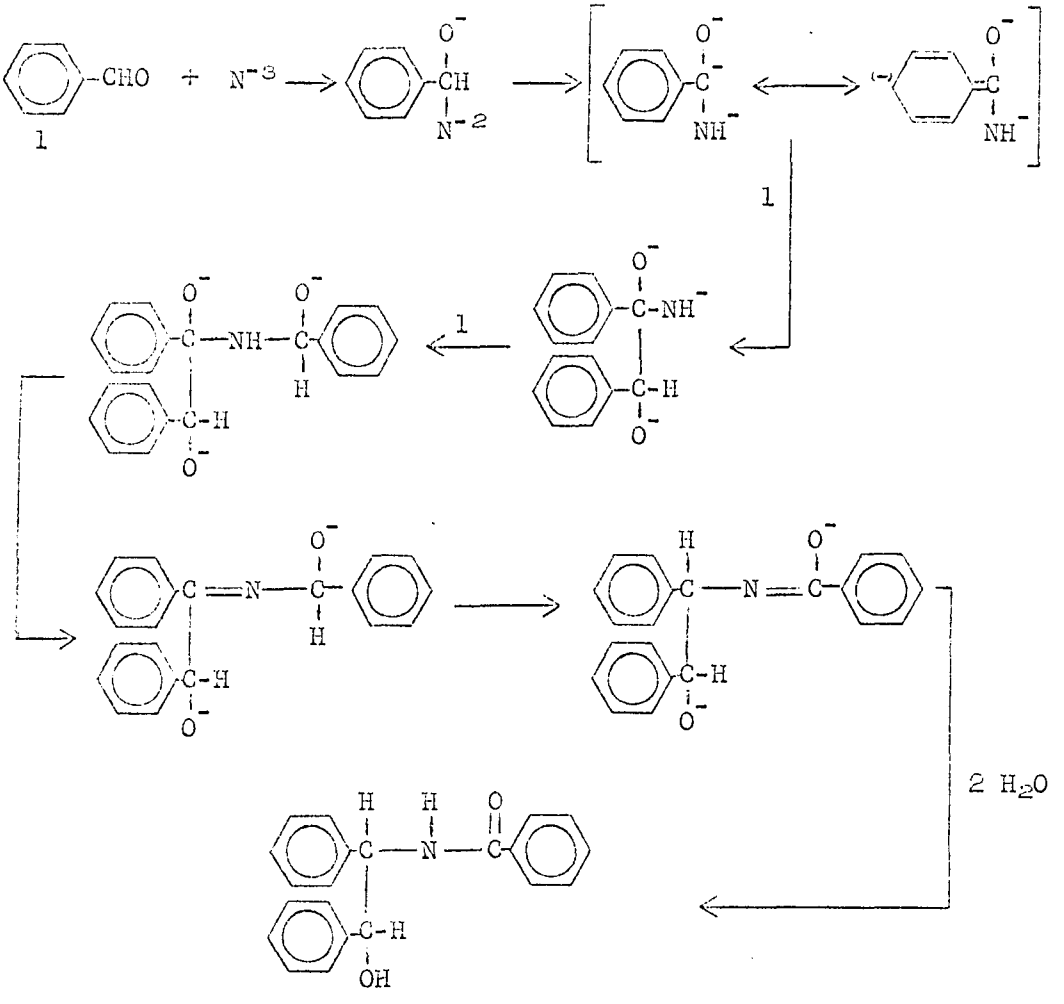
threo-N-(2-Hydroxy-1,2-Diphenylethyl)Benzamide(II).

Formation.

Amide II is formed in the reaction of benzaldehyde with lithium nitride in 21% yield (based on lithium nitride). Thin layer chromatography confirms its presence in the original reaction mixture from which it can be recovered by distillation at reduced pressure.

The amide sublimes at high temperature and can be separated either mechanically or by precipitation from the distillate upon addition of methylene chloride.

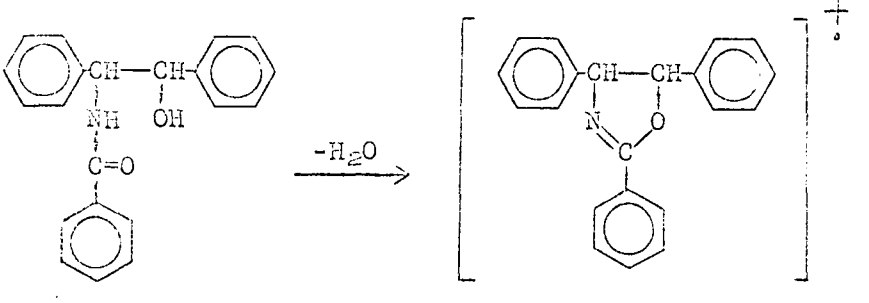
The formation of Amide II may proceed through a benzoin condensation mechanism followed by condensation with benzaldehyde and rearrangement as postulated below:



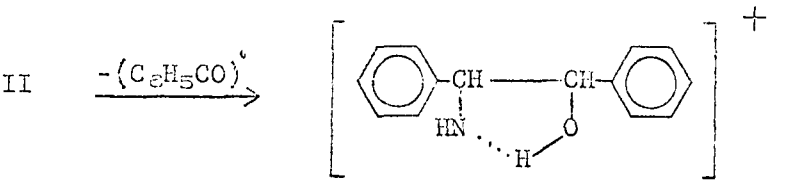
The observation that benzaldehyde reacts with gaseous ammonia to produce hydrobenzamide and none of the Amide II indicates that some other species (N^{-3}, NH^{-2}, NH_2^-, etc.) may well be involved in the formation of Amide II.

Mass Spectrum.

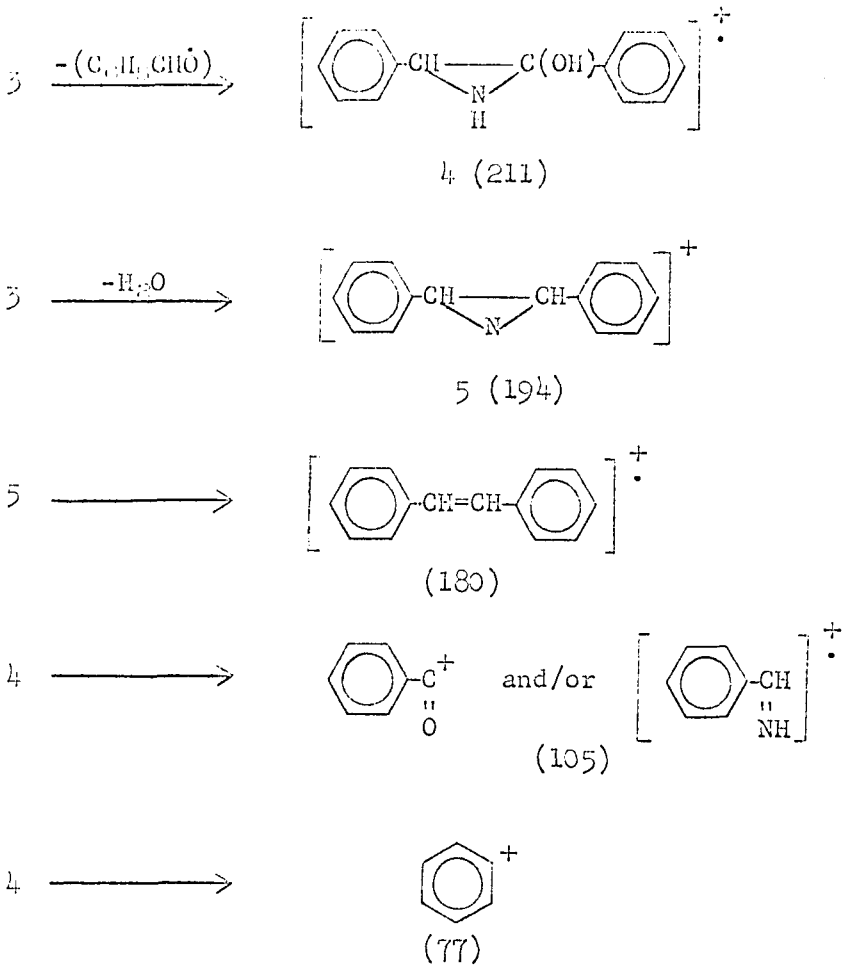
The mass spectrum of Amide II is reproduced in Appendix C, Figure 14. An examination of this spectrum reveals several notable characteristics. Firstly, the absence of a molecular ion (attempts to observe this ion by reduction of the ionizing voltage failed) suggests facile elimination of water with formation of a M^+-18 species. Although supporting data are lacking, this fragment is formulated as the 2,4,5-triphenyl-2-oxazoline radical ion (2) since cyclization-dehydration reactions are common for compounds of this type. Secondly, the similarity of this spectrum with that obtained for the corresponding aminoalcohols and diamine (Appendix C, Figures 15-18) suggest that the 212 (M^+-C_6H_5CO) and/or the 211 (M^+-C_6H_5CHO) fragments are the actual precursors for the lower mass species. On this basis, the spectrum of Amide(II) can be rationalized.



II (317) 2 (299)



3 (212)

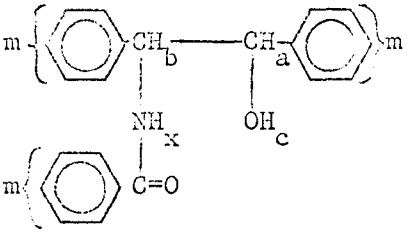


Nuclear Magnetic Resonance Spectrum.

In the characterization of Amide II, difficulty was encountered in interpreting the observed nmr spectrum (Appendix D, Figure 19). Initially it was proposed that Amide II was not pure, but a mixture of two or more components. Thin layer chromatography utilizing various developing solvents ruled out this possibility and pointed to the existence of an equilibrium between two or more conformers. Solvent dependence of the observed nmr spectrum also suggested this possibility.

On the basis on nmr, ir, and mass spectral data as well as other physical properties, the structure of Amide II was postulated as threo-N-(2-hydroxy-1,2-diphenylethyl)benzamide. Decoupling experiments with a 100 MHz nmr spectrometer appeared at first to eliminate this possibility since irradiation in the amide region (8.6 δ) of the spectrum failed to decouple the hydroxyl proton (5.65 δ). The anticipated rapid exchange between NH and OH was expected to result in decoupling of the hydroxyl proton also. However, direct evidence of very slow exchange of the hydroxyl proton was obtained by the addition of deuterium oxide to Amide II dissolved in DMSO-d_6 (Appendix D, Figure 19). Rapid loss of the amide proton signal (5 mins.) with very slow loss of the hydroxyl proton signal (4 hrs.) was observed.

The identity of Amide II as threo-N-(2-hydroxy-1,2-diphenylethyl)benzamide was confirmed by independent synthesis of this amide from threo-1,2-diphenyl-2-aminoethanol[20] by the method of Soderbaum.[31] The nmr assignments are:



H_a - 5.05 δ (broadened t, J_{AB} = 7 Hz, J_{AC} = 6 Hz, 1 H).

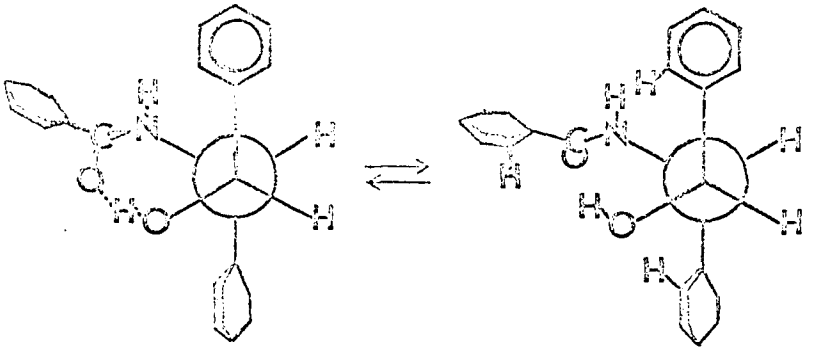
H_b - 5.35 δ (broadened t, J_{AB} = 7 Hz, J_{BX} = 8 Hz, 1 H).

H_c - 5.7 δ (d, J_{AC} = 6 Hz, 0.4 H).

H_m - 7-8 δ (m, 15 H).

H_x - 8.6 δ (d, J_{BX} = 8 Hz, 1 H).

Integration values indicate as much as 40% of Amide II exists in a conformation which restricts hydrogen exchange and hydrogen bonding of the hydroxyl proton while the remainder is in a conformation which allows both. The downfield shift and broadening associated with this hydrogen bonding could account for the fact that only a part of the -OH signal is observable. Framework molecular models indicate that two conformers of Amide II should be favored (fewest non-bonded interactions). These are represented below by Newman projection formulas.



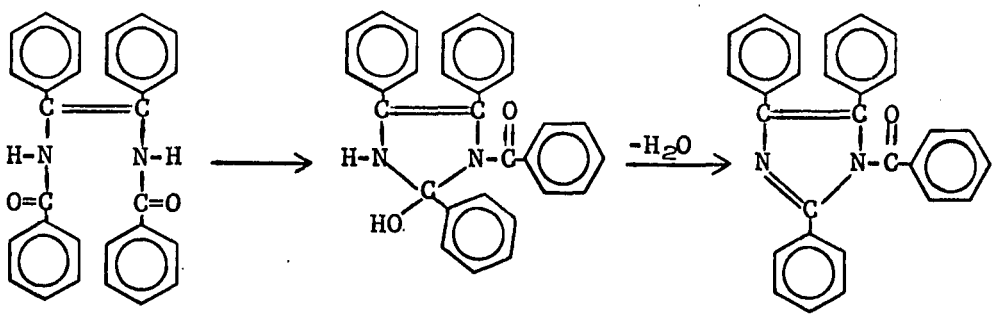
A B

In conformer A, added stability is gained by intramolecular hydrogen bonding with formation of a 7-membered ring. Conversion into conformer B is realized by rotation about the amide linkage. This rotation, as a result of the partial double-bond character of the amide linkage and the geometry of the molecule would be hindered at ordinary temperatures. (Evidence of this was obtained by the observation of a

dependence of the nmr spectrum on temperature). In B the hydroxyl proton is surrounded by the ortho hydrogens of the phenyl rings. These hydrogens could effectively shield the hydroxyl proton from solvent molecules and therefore account for its position in the spectrum and the non-dependence of this position on concentration.

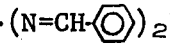
Properties and Structure of Amides I and III.

N-(2-Benzamido-1,2-diphenylethenyl)benzamide(I) and N-(2-toluamido-1,2-bis-p-tolylethenyl)toluamide(III) are insoluble in most common organic solvents, slightly soluble in weak acids and very soluble in strong protonizing acids such as concentrated sulfuric acid. As a result of this insolubility, these amides exhibit remarkable chemical stability under ordinary reaction conditions. For example, they are resistant to base hydrolysis even under the most severe conditions. They do, however, show a marked tendency toward oxidative cleavage in acid media and toward cyclization with formation of the corresponding triarylimidazoles and oxazoles. The formation of the triarylimidazoles, together with the facile loss of water under mass spectral and DTA conditions led to assignment of the cis structure for these amides.

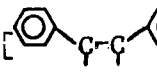


Direct confirmation of this assignment was sought by comparison with the mass spectral properties of both the cis and trans unsubstituted ethenylbisbenzamides; N-(2-benzamidoethenyl)benzamide. Both isomers, however, gave the same mass spectrum with no evidence of facile loss of water (M^+-18) observed. cis-N-(2-Benzamidoethenyl)-benzamide, known to isomerize to the more thermally stable trans-isomers upon heating,[27] evidently isomerizes prior to fragmentation.

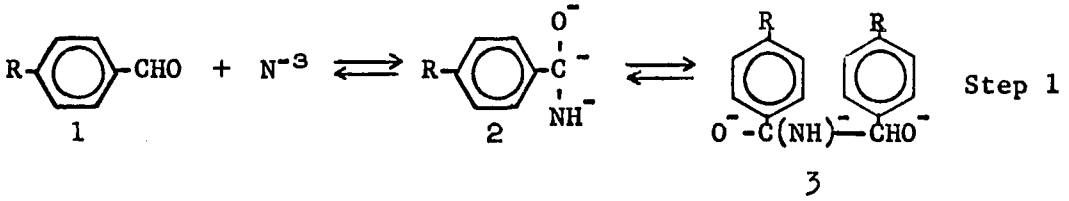
Formation of Amides I and III and Triarylimidazoles IV and V.

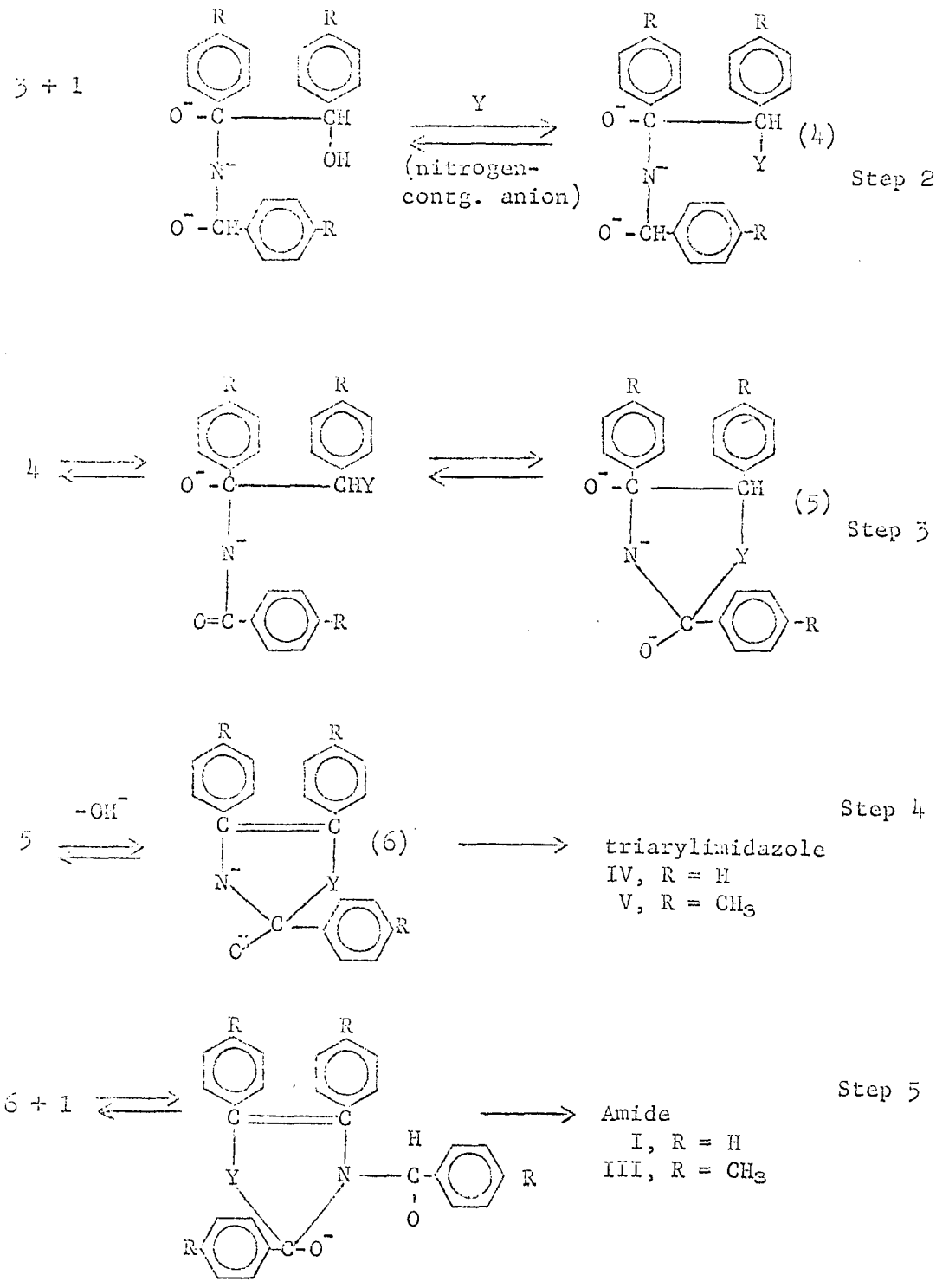
Although Amides I and III have not been reported previously, triarylimidazoles have been formed under a variety of conditions. 2,4,5-Triphenylimidazole, for example, has been prepared under the following reaction conditions: from benzil and benzaldehyde in alcohol solution upon treatment with ammonia;[62] from benzoin in alcohol upon treatment with ammonia at 100°;[63] by treatment of hydrobenzamide [] with hydrogen chloride;[64] by treatment of hydrobenzamide with base;[65] by dry distillation of hydrobenzamide;[66] by treatment of N-desylbenzamide with ammonium acetate in acetic acid;[21] by treatment of N-desylbenzamide with potassium amide in liquid ammonia at elevated temperatures;[67] and by treatment of benzaldehyde with nitrogen sulfide (N_4S_4).[68]

In the reaction of aromatic aldehydes with lithium nitride triarylimidazoles and amides corresponding to Amide I are produced in substantial yields. From the very nature of these products, the reaction paths which lead to their formation must be complex and the elucidation of these mechanisms a formidable task. Similarities in structure

are notable [], and the formation of only the cis isomer (tlc) of Amides I and III suggests the possibility of concurrent formation of the amide and triarylimidazole from a common intermediate or the conversion of one compound into the other. That Amides I and III are converted by either thermal or chemical means into 2,4,5-triarylimidazoles, suggests the latter possibility. However, conditions necessary for effecting these conversions are somewhat extreme and no evidence for their occurrence under reaction conditions could be found. Conversion of the imidazoles into the amides was also considered, since some imidazoles are reported to cleave under Schotten-Baumann benzoylation conditions to yield the corresponding amides. For example, imidazole upon treatment with benzoyl chloride and sodium hydroxide cleaves to produce cis-N-(2-benzamidoethenyl)-benzamide.[69] No reports of similar cleavage of TPI or TTI could be found in the literature and all attempts made in this laboratory also met with failure.

It therefore appears likely that formation of both the amides and the imidazoles proceeds through a common intermediate. This intermediate must be labile and account for exclusive formation of the cis isomer of the amide. One possible mechanism, given below, includes a cyclic intermediate (6) formed from cyclization and partial dehydration of a benzoin-benzaldehyde condensation product.




3 + 1
Y
(nitrogen-contg. anion)
(4)
Step 2
4
(5)
Step 3
5
-OH⁻
(6)
triarylimidazole
IV, R = H
V, R = CH3
Step 4
6 + 1
Amide
I, R = H
III, R = CH3
Step 5

In step 1 of the above mechanism, a molecule of benzaldehyde is adsorbed on the surface of the lithium nitride in the vicinity of the nitride ion and reacts to form the immobile trinegative species (2). Another molecule of benzaldehyde, adsorbed on the surface at a neighboring lithium ion and rendered more electron deficient at the carbonyl carbon by lithium-oxygen interaction [Ar-$\overset{\delta+}{C}$H---O---Li^{+}] is attacked by this trinegative ion forming 3. Condensation of 3 with another molecule of benzaldehyde and subsequent displacement of hydroxyl ion produces 4 (Step 2). Cyclization (Step 3) yields 5, which upon elimination gives 6. This cyclic intermediate (6)*, with the required cis orientation then can form the corresponding imidazole (step 4) or add another molecule of aldehyde ultimately cleaving to give the amide (Step 5).

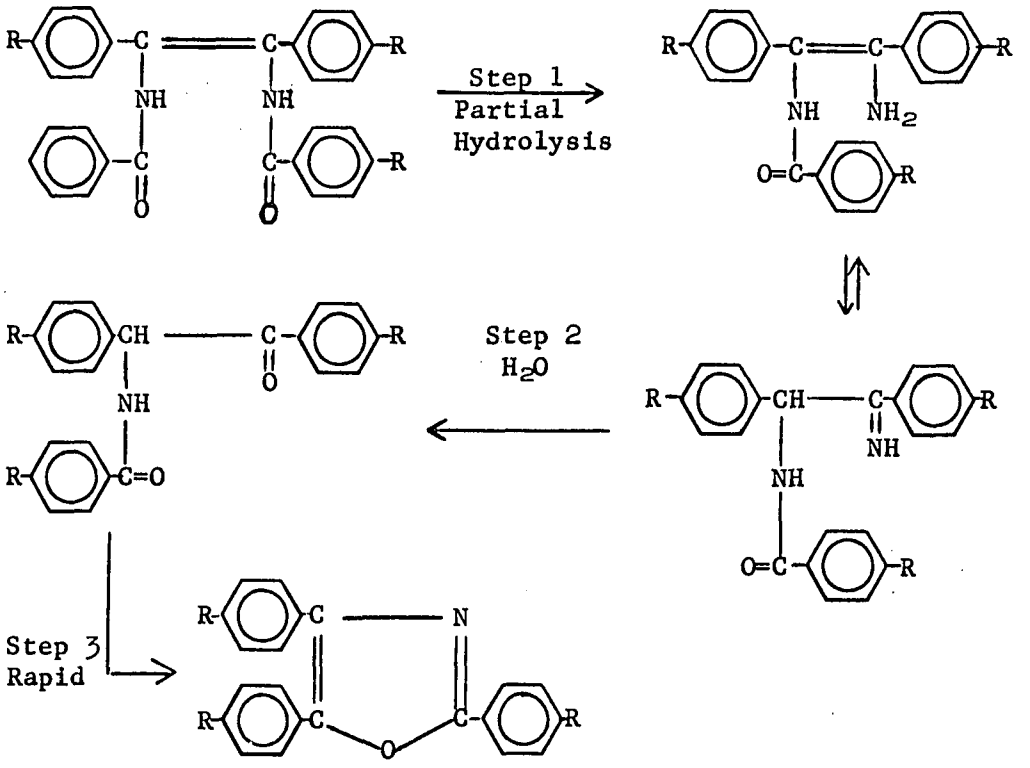
Hydrolysis of Amides I and III.

Amides I and III under steam distillation conditions react rapidly with hot aqueous sulfuric acid (15 M) to form the corresponding triaryloxazoles and acids in quantitative yield. The acids are recovered from the distillate while the oxazoles are precipitated by dilution of the residue with water.

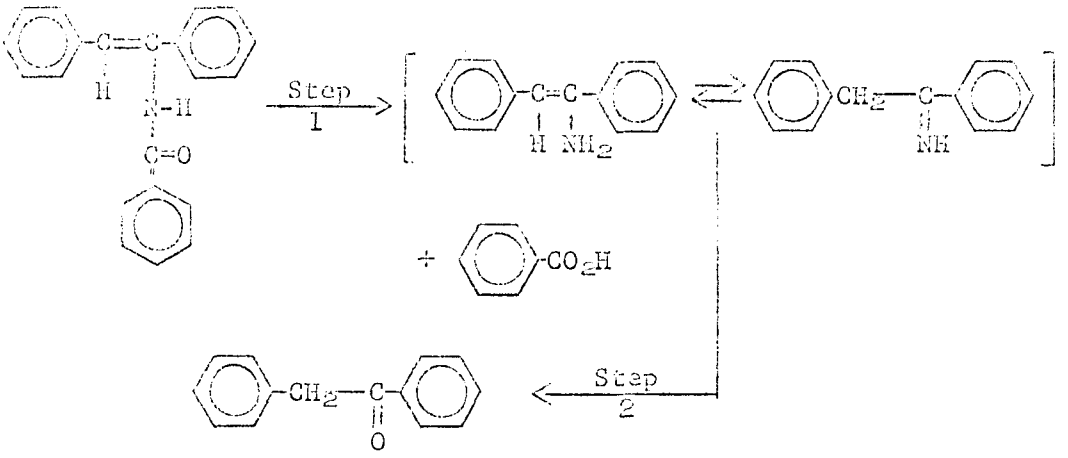
This hydrolysis can be rationalized by the following reaction sequence:

---

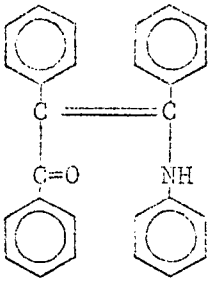
*For a similar intermediate proposed in the formation of imidazoles and oxazoles, see G. McCoy and A. R. Day, J. Am. Chem. Soc., 65, 2169 (1943).



In the presence of sulfuric acid, the amide partially hydrolyzes (Step 1) to form the corresponding imine. These hydrolysis conditions are similar to those used by Irvings and Parkins[42] in the preparation of meso-1,2-diphenylethylene diamine by the acid hydrolysis of meso-N-(2-benzylideneamino-1,2-diphenylethyl)benzamide. The relevance of Steps 1 and 2 of the above sequence in the hydrolysis of Amides I and III is best appreciated by consideration of the steam distillation of N-(1,2-diphenylethenyl)benzamide in aqueous sulfuric acid to yield benzoic acid and desoxybenzoin. Desoxybenzoin results from the hydrolysis of the corresponding imine, produced in the initial reaction (Step 1).



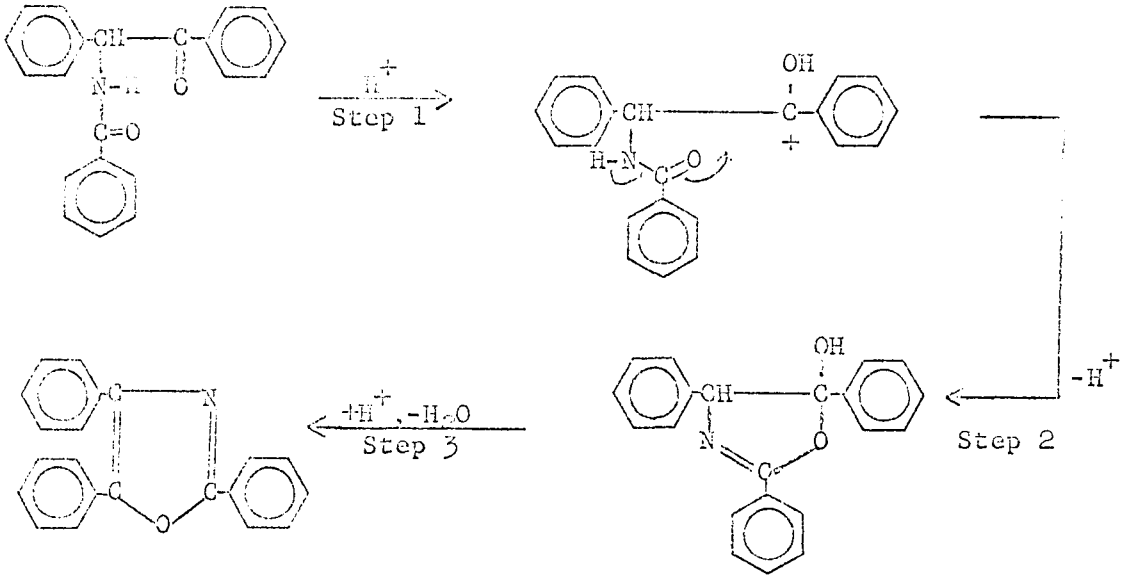
A similar hydrolysis, no doubt proceeding by an analogous mechanism, was reported by Wasserman and Liberles[70] in 1960. They noted that N-(2-benzoyl-1,2-diphenylethenyl)benzamide readily hydrolyzed to produce dibenzoylphenyl methane.



Step 3, the cyclization-dehydration of the corresponding N-desylbenzamides in sulfuric acid is an example of one of the best methods of producing substituted oxazoles, namely the cyclization of α-acylamino ketones, employing the Robinson-Gabriel Synthesis.[71] The earliest example of this cyclization reaction was reported by Laurent[66] who obtained 2,4,5-triphenyloxazole in quantitative yield by the action of sulfuric acid on N-desylbenzamide exactly as proposed above.

Evidence that this cyclization reaction is rapid and proceeds before further hydrolysis or decomposition can occur is furnished by McKenzie and Barrow[72] who report the quantitative cyclization of N-desylbenzamide upon treatment with warm sulfuric acid for two minutes.

To date, no mechanistic work has been reported on this interesting cyclization reaction; however, it appears reasonable that the reaction proceeds by the following path.[73]

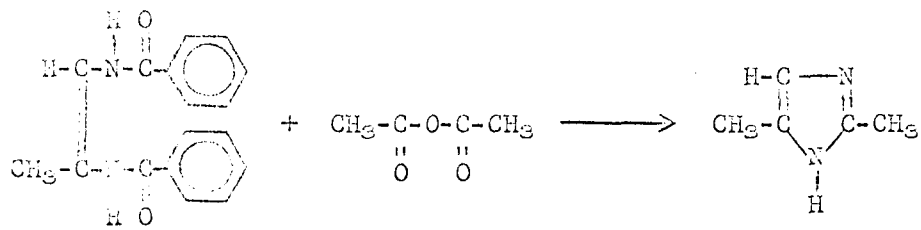


In the initial step, protonation of the keto carbonyl in acid medium could induce addition of the α-acylamino oxygen to the electron deficient carbonyl carbon (Step 2). Loss of a molecule of water would produce the corresponding oxazole (Step 3).

Cyclization Reactions of Amides I and III.

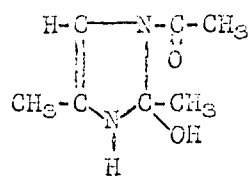
Amides I and III are readily converted by thermal or chemical means into the corresponding triarylimidazoles IV and V. Addition of I to refluxing benzoyl chloride or benzoic anhydride results in the

formation of 2,4,5-triphenylimidazole in quantitative yield. Other examples of cyclization reactions under similar conditions have been reported. For example, addition of N-(2-benzamido-2-methylethenyl)-benzamide to refluxing acetic anhydride results in the formation of 2,4(or 5)-dimethylimidazole according to the following equation.[74]

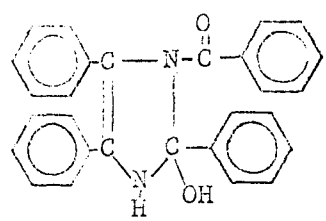


1

Transacylation of 1, followed by cyclization, would yield



which, by elimination of acetic acid would give the corresponding imidazole. By analogy, Amide I upon cyclization would yield



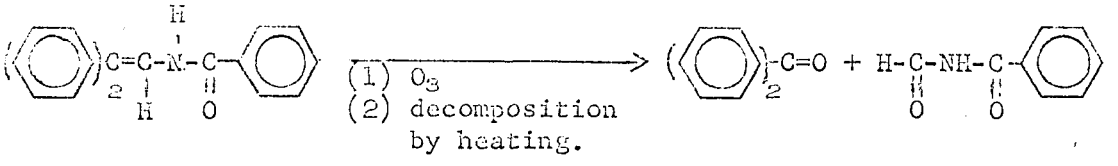
which, by elimination of benzoic acid, would afford the corresponding imidazole.

Pyrolysis of Amides I and III by heating to 300° led to formation of the corresponding imidazoles in near quantitative yield.

Although some decomposition occurs, as noted by the presence of the corresponding nitrile in the distillate, the reaction, no doubt, proceeds through a cyclic intermediate as proposed above. As expected, the corresponding acid and anhydride can also be detected in the distillate.

Ozonolysis of Amide I in Formic Acid.

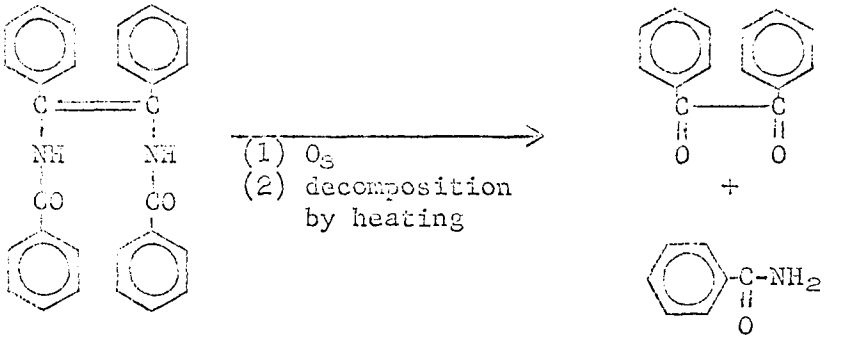
Benzil and benzamide are produced upon treatment of Amide I with excess ozone in 97% formic acid according to the method of Krabbe, Dohlk and Schmidt.[75] The selection of formic acid as solvent was based on several considerations. Firstly, ozonolysis of somewhat similar compounds was reported in this solvent. N-(2,2-Diphenylethenyl)-benzamide, for example, gave benzophenone (82% yield) and N-formylbenzamide (41% yield) when treated with ozone in formic acid.[75]



Secondly, of the possible solvents, formic acid offered the best possibility of success due to the solubility (albeit slight) of Amide I in this solvent. And thirdly, formic acid has the ability to limit oxidation of olefinic linkages to the corresponding carbonyl as is evidenced above by the formation of N-formylbenzamide and as cited by Dorland and Hibbert[76] among others. In their hands, maleic acid is converted into glyoxylic acid in 98% yield, while in the usual ozonolyses solvents further oxidation to oxalic acid predominated. This selectivity is attributed to the immediate decomposition of the ozonide by

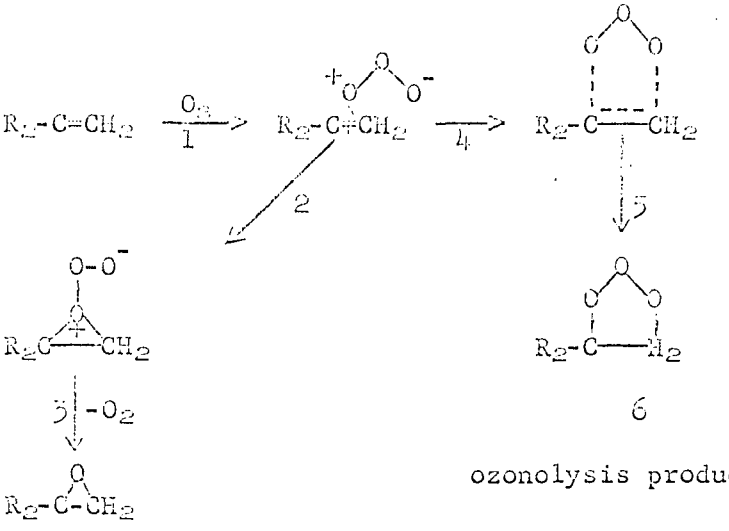
the residual water present in the acid and to its ability to react with peroxidic products with formation of carbon dioxide.

The conversion of Amide I into benzil and benzamide is an example of "partial" double bond cleavage during ozonolysis[77]

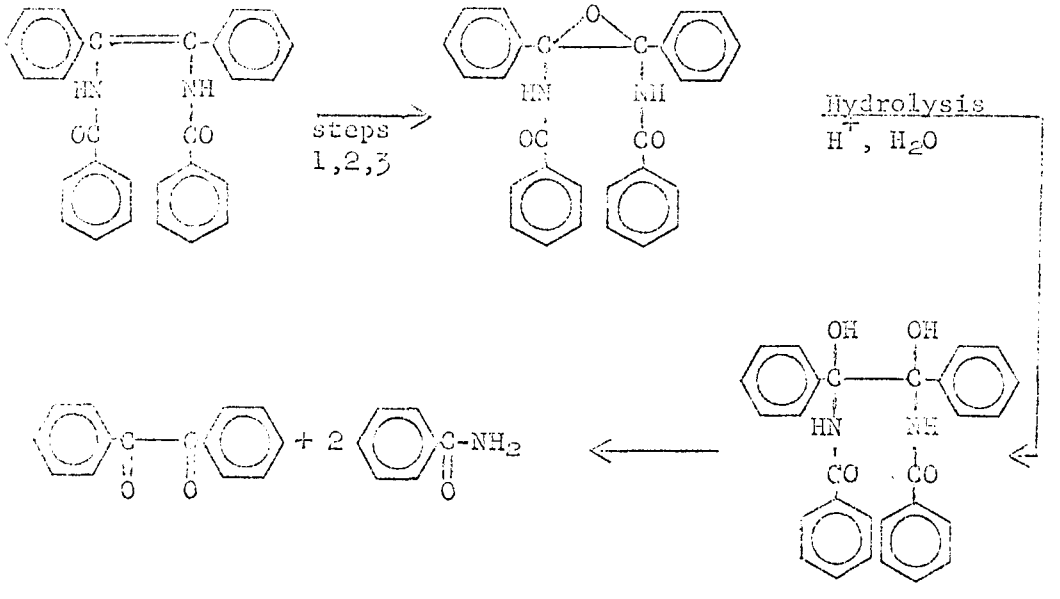


which is common among sterically hindered olefins. Ozonolysis of sterically hindered olefins usually yields epoxide, rearranged or hydrolysis products. 3,3,4,4-Tetramethyl-2-t-butylpentene-1 $(CH_3)_3-C-C(CH_3)_2-C(=CH_2)-C(CH_3)_3$ upon treatment with ozone afforded the corresponding epoxide in 50% yield,[78] while 1-mesityl-1-phenylethylene gave the corresponding 2-mesityl-2-phenylvinyl alcohol as the predominant ozonolysis product.[79]

Competition between partial cleavage and ozonolysis is presently explained by the following mechanism.[80]



Initial attack by ozone (Step 1) on an olefinic double bond involves formation of a π complex which can either proceed into a 1,3-dipolar cycloaddition reaction (Step 4) to give normal ozonolysis products or, if the olefin is sufficiently hindered, to a σ complex (Step 2) followed by loss of oxygen (Step 3) to give partial cleavage products. On this basis, ozonolysis of Amide I is rationalized.

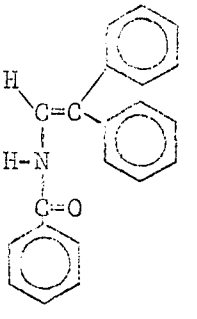


Oxidation of Amide I with Potassium Dichromate in Glacial Acetic Acid.

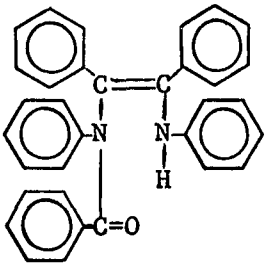
Oxidation of Amide I with potassium dichromate was conducted in glacial acetic acid because of the solubility (albeit slight) of the amide in this solvent. The main product of this oxidation was dibenzamide; produced as expected by cleavage of the olefinic bond in the molecule. Small amounts of benzil were isolated from the reaction mixture, formed by cleavage of the nitrogen-carbonyl carbon bond followed by hydrolysis. Benzil could also have been formed by simple hydrolysis of Amide I; however, this possibility is not likely since Amide I is resistant to hydrolysis under the reaction conditions. All attempts to eliminate the formation of benzil completely were unsuccessful.

Using somewhat similar conditions, Einhorn[81] in 1905, had investigated the potassium dichromate oxidation of N-hydroxymethyl benzamide in dilute sulfuric acid. He also observed nitrogen-carbon bond cleavage with the formation of benzamide.

Krabbe, Bohlk and Schmidt,[75] however, reported only carbon-carbon double bond scission in the acid catalyzed permanganate oxidation of N-(2,2-diphenylethenyl)benzamide.



N-(2-anilino-1,2-diphenylethyl)benzanilide

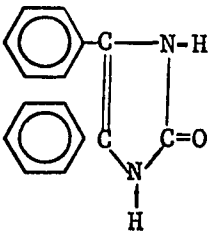


has been observed to undergo oxidation under mild conditions at the carbon-carbon double bond with the formation of dibenzanilide and benzanilide.[82]

Oxidation of Amide I with Bromine in Glacial Acetic Acid.

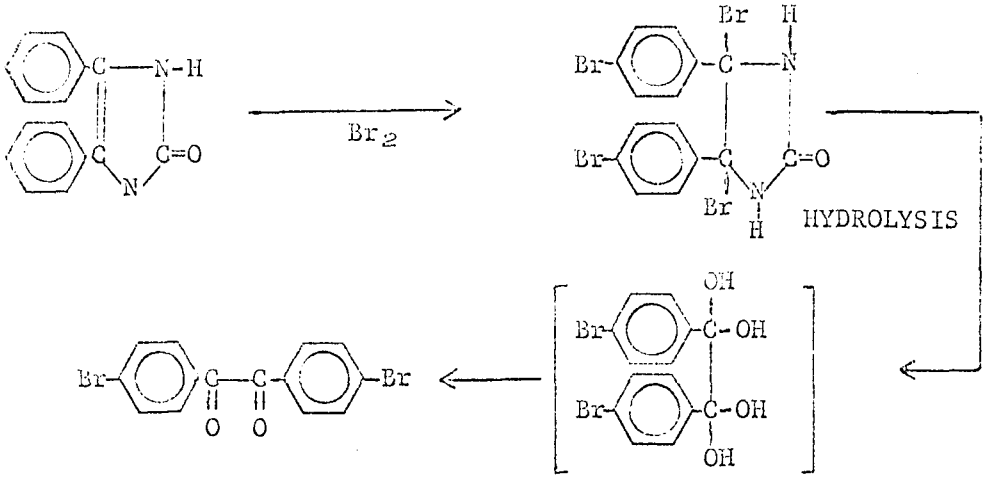
Amide I reacts rapidly with bromine in glacial acetic acid to produce benzil, benzamide and benzoic acid. The observed molar ratio of benzil to benzamide and benzoic acid (benzamide has been shown to hydrolyze rapidly under the reaction conditions) produced in the oxidation is 1:2.

A reaction quite similar to this was reported by H. Biltz[83] in 1908. Elemental bromine, in large excess, was observed to react with 4,5-diphenylimidazolone



in refluxing glacial acetic acid to produce, upon hydrolysis, p,p'-dibromobenzil. Formation of the substituted benzil is postulated to

occur by addition of bromine across the carbon-carbon double bond followed by hydrolysis of the 1,2-dibromide.



An analogous mechanism could account for the formation of benzil and benzamide from Amide I.

Many other examples of oxidations of amides have been reported in the literature with initial attack occurring at the carbon atom alpha to the amide nitrogen. Photochemical oxidation of N-alkylamides[84,85] and reaction of N,N-dimethylacetamide with peracetic acid has also been shown to proceed at the methyl carbon of the amine.[86]

Mass Spectra of Ethenyl-bis-Amides.

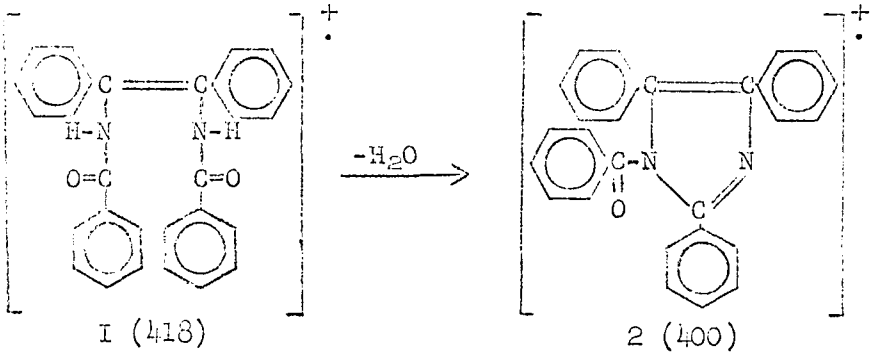
The mass spectra of cis-N-(2-benzamido-1,2-diphenylethenyl)-benzamide(I), cis-N-(2-toluamido-1,2-bis-p-tolylethenyl)toluamide(III), trans-N-(2-benzamidoethenyl)benzamide and cis-N-(2-benzamidoethenyl)-benzamide are reproduced in Appendix C, Figures 11-14, respectively.

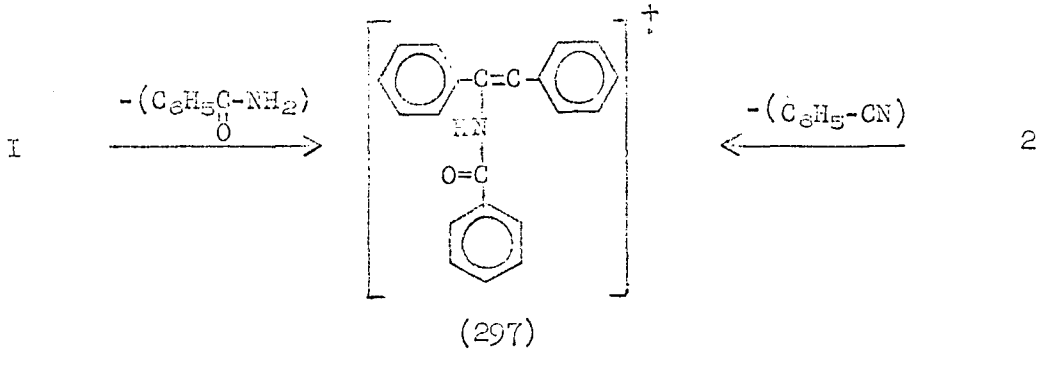
Similarities are evident in the spectra of Amides I and III. The appearance of a M^+-18 fragment in both spectra is of particular

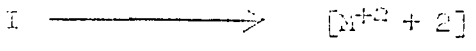
significance since it presumably represents the formation of the corresponding imidazole by cyclization-dehydration of the respective cis-amide. cis- and trans-N-(2-Benzamidoethenyl)benzamide produce identical fragmentation patterns and fail to give the M^+-18 species characteristic of the cis conformation. The cis isomer under mass spectral conditions must isomerize to the more thermally stable trans form prior to fragmentation.

The fragmentation of these ethenyl-bis-amides is considered below.

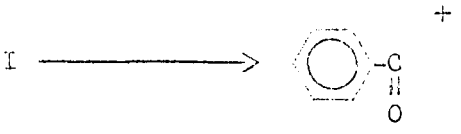
Amide I.







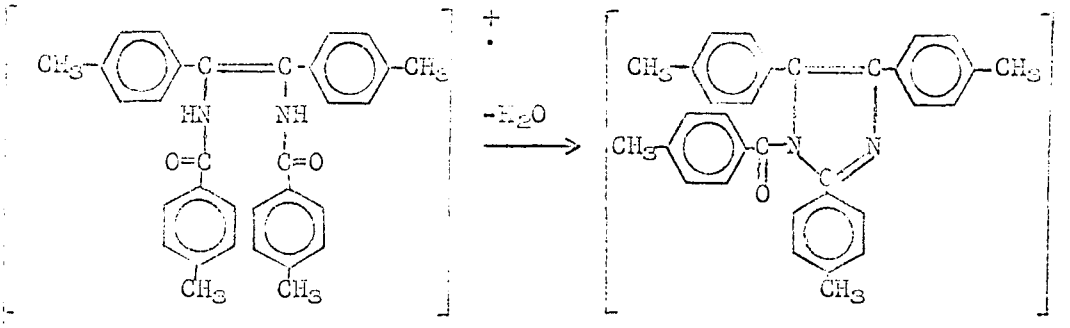
(210)



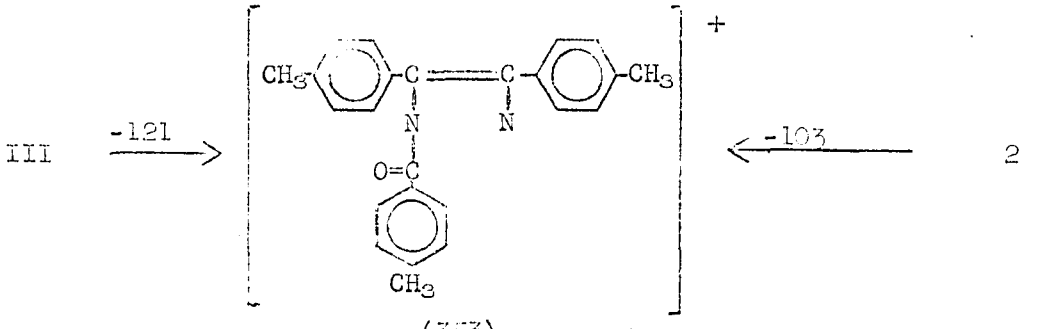
(105)

(77)

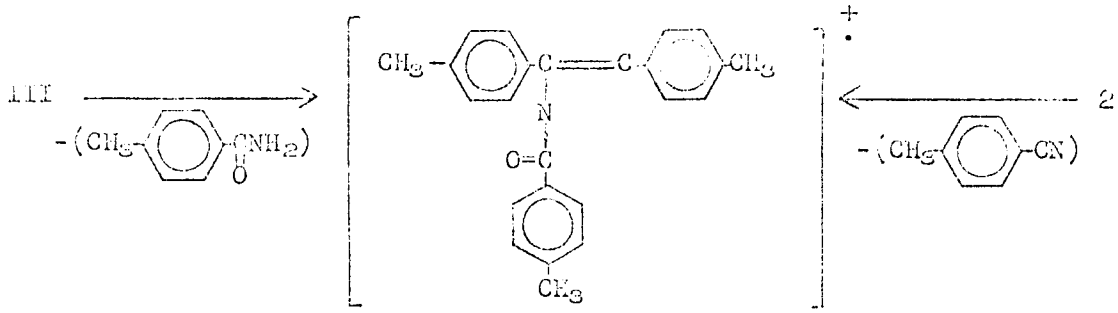
Amide III.



III (474) 2, (456)



(353)



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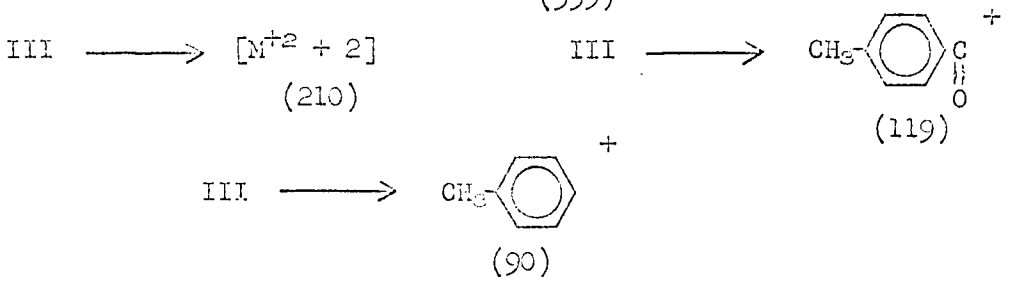
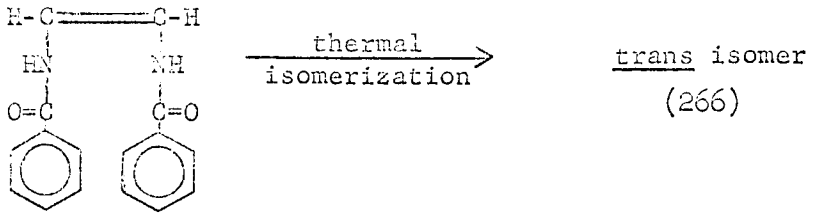


(210)

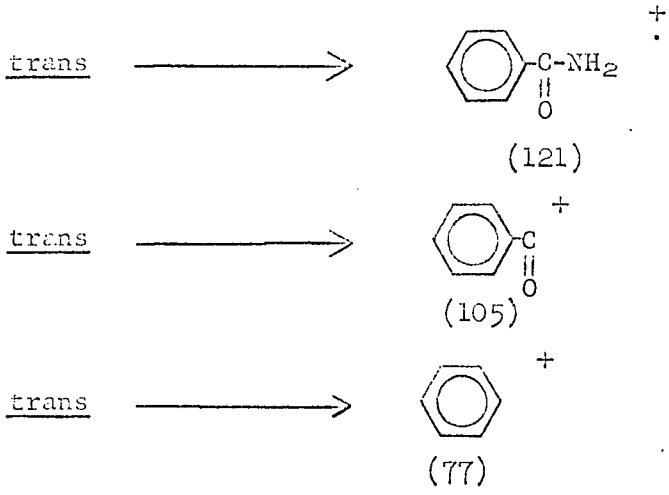
(119)

(90)

cis and trans-N-(2-Benzamidoethenyl)Benzamide.



(266)



(121)

(105)

(77)

CONCLUSIONS

Aromatic aldehydes have been shown to react with lithium nitride to produce a complex series of compounds resulting from Tischenko, Cannizzaro, benzoin condensation, elimination and cyclization reactions. With benzaldehyde, there are produced ammonia, benzyl benzoate, benzyl alcohol, benzoic acid salts, cis-N-(2-benzamido-1,2-diphenylethenyl)benzamide, threo-N-(2-hydroxy-1,2-diphenylethyl)-benzamide, 2,4,5-triphenylimidazole and benzamide. With p-tolualdehyde, the reaction products include ammonia, p-xylyl p-toluate, p-methylbenzyl alcohol, ammonium p-toluate, cis-N-(2-toluamido-1,2-bis-p-tolylethenyl)toluamide, 2,4,5-tris-p-tolylimidazole and p-xylyl p-toluamide.

Although most of the products isolated can be produced by more efficient methods, this reaction of aromatic aldehydes with lithium nitride serves as a convenient method of producing the corresponding diarylethenyl-bis-amides in acceptable yield. This largely neglected series of bis-amides, whose unusual physical and chemical characteristics will no doubt generate some interest, are readily accessible by this simple procedure.

APPENDIX A

Analytical Methods

Thin Layer Chromatography of the Reaction Products of Benzaldehyde and p-Tolualdehyde with Lithium Nitride.

Thin layer chromatography was used to study the reaction products of benzaldehyde and p-tolualdehyde with lithium nitride.

Experimental.

Silica Gel G (30 g.) was mixed with water (65 ml.) and applied in the usual manner to glass plates (0.5 mm. layer) using a Desaga spreader. The plates were dried for 0.5 hr. at room temperature and then activated overnight at 130°. Spot detection was normally accomplished by uv induced luminescence or iodine staining.

TABLE IV

SELECTION OF A SUITABLE SOLVENT

Solvent System	Rf		
	2,4,5-Triphenylimidazole	N-(2-Benzamido-1,2-diphenylethenyl)-benzamide	Benzamide
Cyclohexane-ethyl acetate (90:10)		0.0	
Toluene-ethanol (1:1)	0.90	0.90	0.50
Toluene-ethanol (75:25)	0.73	0.80	0.51
Cyclohexane-toluene-ethanol (25:50:25)	0.67	0.91	0.43
Cyclohexane-toluene-ethanol (40:40:20)	0.67	0.89	0.42
Cyclohexane-benzene-ethanol (77:20:3)	0.12	0.18	0.03
Cyclohexane-benzene-ethanol (65:25:10)	0.50	0.51	0.23

TABLE V

Compounds of Interest	Rf in Cyclohexane-benzene-ethanol (65:25:10)	Rf in Cyclohexane-ethyl-acetate (90:10)	Detection	
			uv	I_2
N-(2-benzamido-1,2-diphenyl-ethenyl)benzamide	0.45	0.00	slt. blue	----
2,4,5-triphenylimidazole	0.43	----	blue	dark
benzamide	0.19	0.00	dark	dark
benzoic acid	----	0.05	----	----
benzyl alcohol	0.55	0.13	----	dark
dibenzamide	0.71	0.00	----	dark
benzyl benzoate	0.72	0.54	slt. blue	dark
threo-N-(2-hydroxy-1,2-diphenyl-ethyl)benzamide	0.31	0.00	----	dark
benzaldehyde	0.55	0.39	dark	dark
2,4,5-triphenyloxazole	----	0.10	----	dark
hydrobenzamide	----	0.45	dark	dark
benzoin	----	0.10	----	dark
benzonitrile	----	0.50	----	dark

TABLE VI

Compounds of Interest	Rf in Cyclohexane-benzene-ethanol (65:25:10)	Rf in Cyclohexane-ethyl-acetate (90:10)	Detection	
			uv	I_2
ammonium-p-toluate	0.05	0.00	----	dark
p-methylbenzyl alcohol	0.42	0.15	dark	dark
2,4,5-tris-p-tolylimidazole	0.45	0.25	brt. blue	dark
p-xylyl p-toluate	0.68	0.55	lt. blue	dark
p-xylyl p-tolamide	0.38	----	dark	dark
p-tolylaldehyde	0.60	0.50	dark	dark
N-(2-toluamido-1,2-bis-p-tolylethenyl)toluamide	0.47	0.00	----	dark

TABLE VII

TLC OF BENZALDEHYDE REACTION MIXTURE

Rf with Cyclohexane-benzene-ethanol (65:25:10)	Characteristics		Identification by TLC
	uv	I_2	
0.76	lt. blue	dark	benzyl benzoate
0.60	lt. yellow	dark	benzaldehyde
0.54	----	dark	benzyl alcohol
0.50	lt. blue	----	N-(2-benzamido-1,2-diphenylethenyl)benzamide
0.45	brt. blue	dark	2,4,5-triphenylimidazole
0.28	----	dark	threo-N-(2-hydroxy-1,2-diphenyl)benzamide
0.21	slt. yellow	dark	benzamide
0.05	----	dark	ammonium benzoate

TABLE VIII

TLC OF p-TOLUALDEHYDE REACTION MIXTURE

Rf with Cyclohexane-benzene-ethanol (65:25:10)	Characteristics		Identification by TLC
	uv	I_2	
0.68	lt. blue	dark	p-xylyl p-toluate
0.62	dark	dark	p-tolualdehyde
0.55	----	dark	N-(2-toluamido-1,2-bis-p-tolylethenyl)toluamide
0.51	----	dark	p-methylbenzyl alcohol
0.45	brt. blue	dark	2,4,5-tris-p-tolylimidazole
0.40	----	dark	p-xylyl p-toluamide
0.51	----	dark	ammonium p-toluate

Gas Chromatographic Analysis of the Products of Reaction Between Benzaldehyde and Lithium Nitride.

A glc method was developed for determining the relative amounts of benzaldehyde, benzyl alcohol and benzyl benzoate in reaction mixtures containing these volatile components by use of diphenyl ether as an internal standard.

Equipment and Materials.

Aerograph autoprep gas chromatograph, Model A-700, equipped with a thermal conductivity detector and a 9' silicone gum rubber column on Chromasorb G support; reagent grade samples of carbon tetrachloride, benzyl alcohol, benzaldehyde, benzyl benzoate and diphenyl ether; a Dietzgen and Co., Planimeter No. 123 A; and a 10 µl Hamilton syringe.

Column Conditions.

Column temperature - 185°

Detector temperature - 255°

Injector temperature - 205°

Helium Pressure - 30 lb

Sample size - 3 µl

Procedure.

Approximately equal quantities of diphenyl ether and stripped reaction mixture are weighed (± 1 mg.) into a small flask. The composite is mixed thoroughly and a 3 µl sample is injected into the gas chromatograph operating under the conditions listed. The relative peak areas of the resulting chromatogram, determined with a planimeter,

are converted into relative weights by multiplication with the appropriate response factors (Table IX). Weight percents can then be calculated in the usual manner.

TABLE IX

RESULTS

Component	Relative Response Factor	Rf values in mins.
Carbon Tetrachloride	1.45	1.2
Benzaldehyde	0.87	2.3
Benzyl Alcohol	1.28	2.8
Diphenyl Ether	1.00	8.1
Benzyl Benzoate	1.04	28.0

Infrared Method for the Semi-Quantitative Determination of the Composition of threo-N-(2-Hydroxy-1,2-Diphenylethyl)Benzamide (Amide II) - Benzyl Benzoate Mixtures.

An examination of the infrared spectra of Amide II and benzyl benzoate, together with known mixtures of the two, indicated a possible correlation between concentration and absorbance at 1630 cm^{-1} (C=O) and at 1720 cm^{-1} (C=O) for amide and ester, respectively. The results obtained for neat smear samples are given in Table X, and plotted in Graph 1.

TABLE X

Mole Fraction of threo-N-(2-hydroxy,1-2 diphenylethyl)benzamide in Benzylbenzoate	Ester Absorbance at 1720 cm^{-1}	Amide Absorbance at 1630 cm^{-1}	Ratio 1630/1720
0.078	0.70 (3)	0.14 (3)	0.20
0.236	0.64 (3)	0.29 (3)	0.453
0.381	0.42 (3)	0.24 (3)	0.575
0.381	0.38 (3)	0.23 (3)	0.605

Infrared Method for the Semi-Quantitative Determination of the Composition of Benzil-Benzamide Mixtures.

A cursory examination of the infrared spectra of pure benzamide and benzil, together with those of known mixtures of the two, indicated a possible correlation between concentration and absorbance at 3390 cm^{-1} (N-H stretch, benzamide) and 1000 cm^{-1} (C-H out of plane bending, benzil). The results obtained for samples run in Nujol mulls are given in Table XI, and plotted in Graph 2.

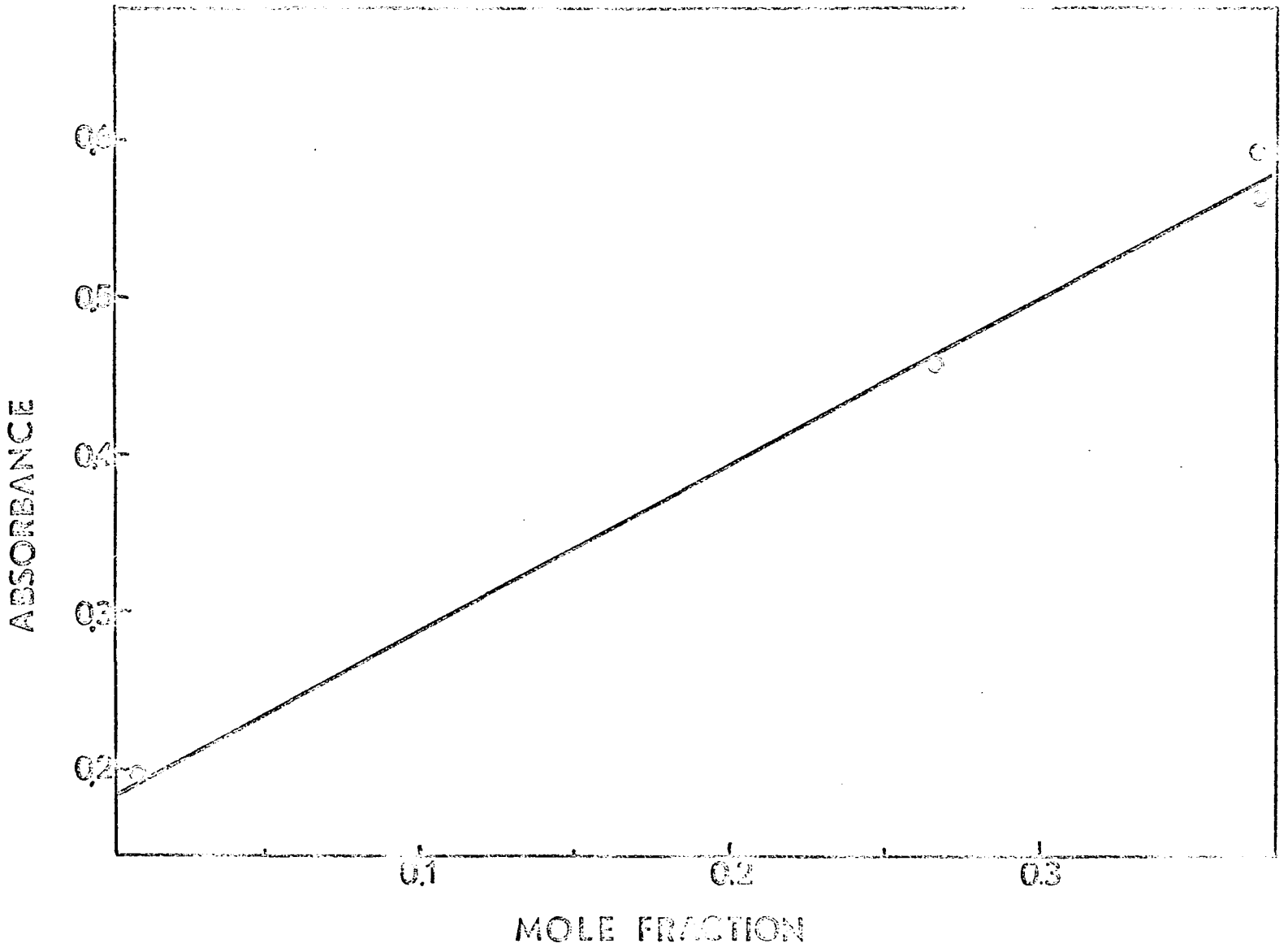
TABLE XI

Mole Fraction of Benzamide in Benzil	Benzamide Absorbance at 3390 cm^{-1}	Benzil Absorbance at 1000 cm^{-1}	Ratio 3390/1000
0.33	0.200 (3)	0.226 (3)	0.88
0.50	0.502 (3)	0.326 (3)	1.54
0.67	0.177 (3)	0.079 (3)	2.24

GRAPH 1

threo-N-(2-HYDROXY-1,2-DIPHENYLETHYL)BENZAMIDE-BENZYL BENZOATE MIXTURES

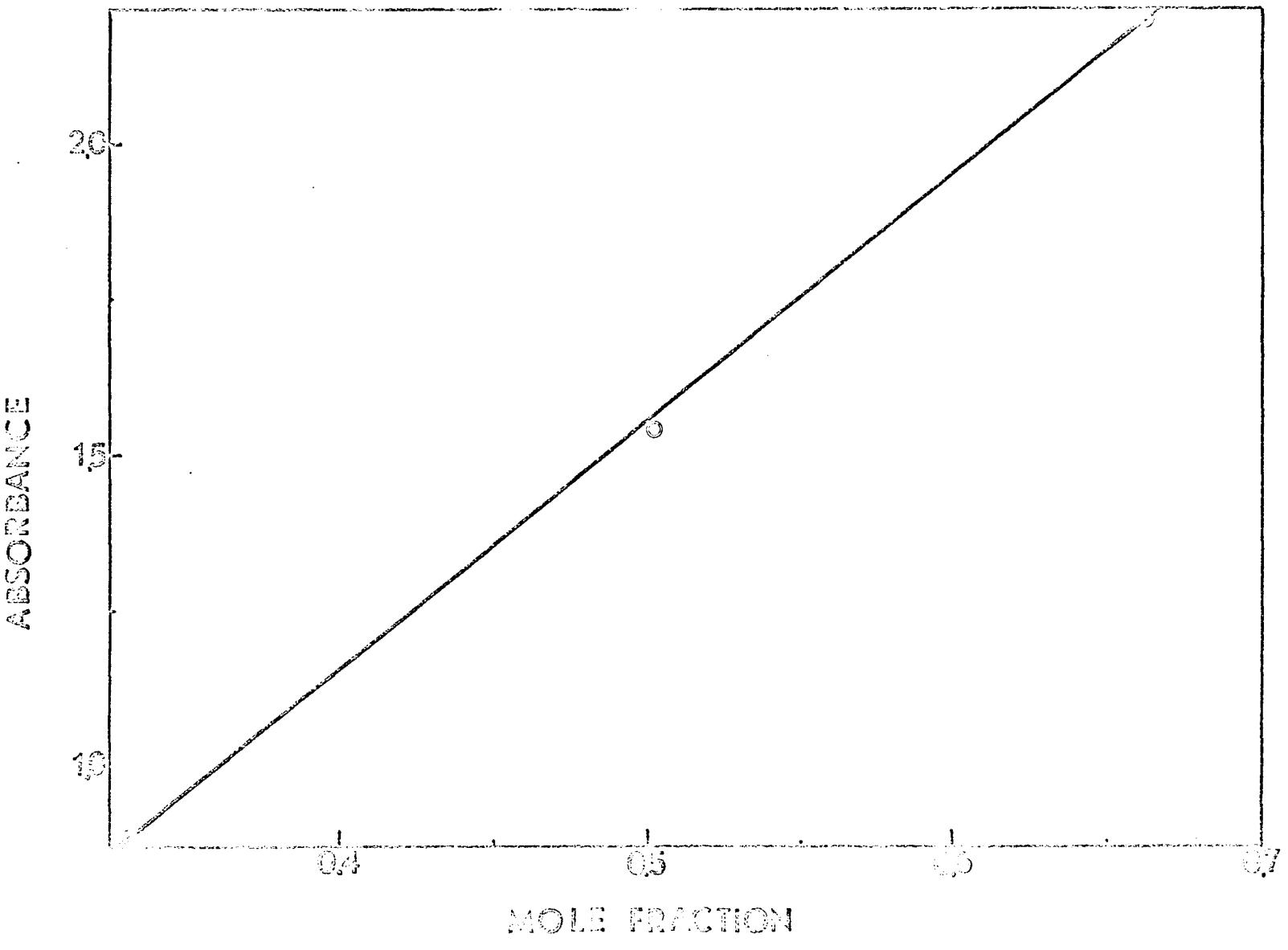
Plot of absorbance ratio at 1630 cm^{-1}: 1720 cm^{-1} versus mole fraction of threo-N-(2-hydroxy-1,2-diphenylethyl)benzamide in benzyl benzoate.


ABSORBANCE
0.2
0.3
0.4
0.5
0.6
0.1
0.2
0.3
MOLE FRACTION

GRAPH 2

BENZIL-BENZAMIDE MIXTURES

Plot of absorbance ratio at 3390 cm^{-1}: 1000 cm^{-1} versus mole fraction of benzamide in benzil.


ABSORBANCE
2.0
1.5
1.0
0.4
0.5
0.6
0.7
MOLE FRACTION

Molecular Weight Determinations in Camphor.

General Procedure.

Freshly sublimed camphor (at 135°) was weighed into test tubes containing a known weight of sample whose molecular weight was to be determined. The camphor and sample were thoroughly mixed and then melted until homogeneous by placing the test tube in an oil bath at 190°. The molten solutions were allowed to solidify and after remixing, the samples were mechanically ground. Capillary tubes were filled with approximately 5mm. of sample and packed uniformly. The capillaries were sealed *in vacuo* at a point approximately an inch from the closed end with care being taken to avoid any overheating of sample during sealing.

To minimize variations in observed melting points, each determination was accompanied by samples of pure, sublimed, melted, ground camphor. Sample sizes were always adjusted as closely as possible and heatup rates were reduced to less than 0.1° C. per min., approximately 2° below the initial melting point of the mixture. (This was possible by use of a Hoover Capillary Melting Point apparatus connected to a variable rheostat). Melting point temperatures, *i.e.*, the disappearance of the last solid crystal, were recorded with the aid of a magnifier to 0.02° by using a 77 mm. immersion thermometer with 0.1° subdivisions.

TABLE XII

MOLECULAR WEIGHT DETERMINATIONS IN CAMPHOR

Sample	Wt. of Sample (g.)	Wt. of Camphor (g.)	Heatup Rate °C/Min.	Avg. ΔT in °C	Avg. Mol. Wt.	Actual Mol.Wt.
N-(1,2-diphenyl-ethenyl)benzamide	0.01115	0.70493	0.1	2.10 (3)	301 (3)	299
N-(2-benzamido-1,2-diphenylethenyl)benzamide	0.0074	0.44525	0.05	1.61 (5)	413 (5)	418
N-(2-benzamido-1,2-diphenylethenyl)benzamide	0.0185	0.9707	0.1	1.83 (5)	407 (5)	
N-(2-benzamido-1,2-diphenylethenyl)benzamide	0.00635	0.52905	0.1	1.24 (5)	412 (5)	
					411 Avg.	
N-(2-hydroxy-1,2-diphenylethyl)benzamide	0.0034	0.2096	0.1	2.3 (1)	282 (1)	317
N-(2-hydroxy-1,2-diphenylethyl)benzamide	0.0040	0.1204	0.1	3.6 (1)	369 (1)	
					326 Avg.	

APPENDIX B

Infrared Spectra

FIGURE 2

Infrared Spectrum (Nujol) of

cis-N-(2-BENZAMIDO-1,2-DIPHENYLETHENYL)BENZAMIDE

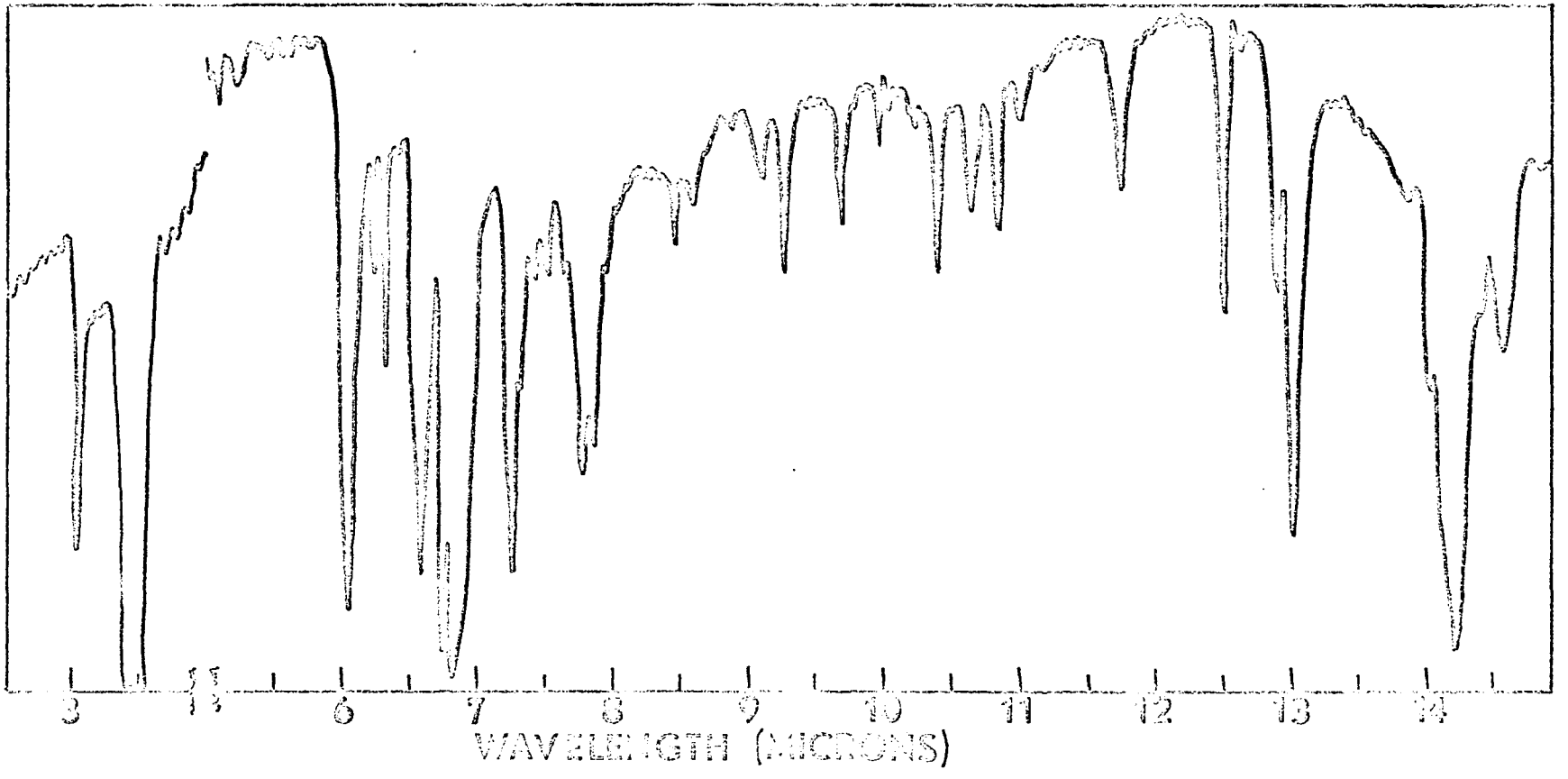

3
6
7
8
9
10
11
12
13
14
WAVELENGTH (MICRONS)

FIGURE 3

Infrared Spectrum (Nujol) of

cis-N-(2-TOLUAMIDO-1,2-BIS-p-TOLYLETHENYL)TOLUAMIDE

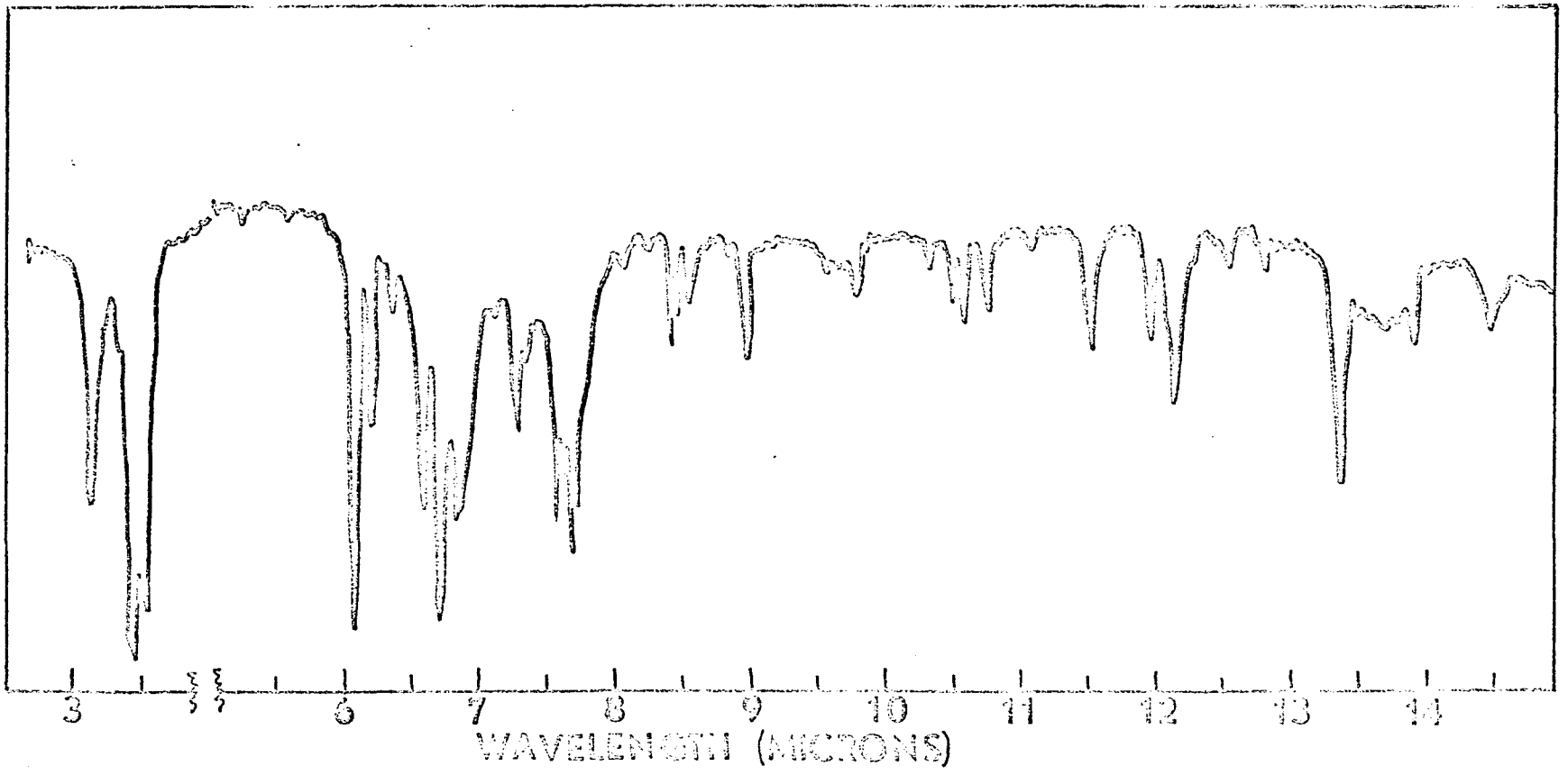

3
6
7
8
9
10
11
12
13
14
WAVELENGTH (MICRONS)

FIGURE 4

Infrared Spectrum (Nujol) of

N-(2-BENZAMIDO-1,2-DIPHENYLETHYL)BENZAMIDE

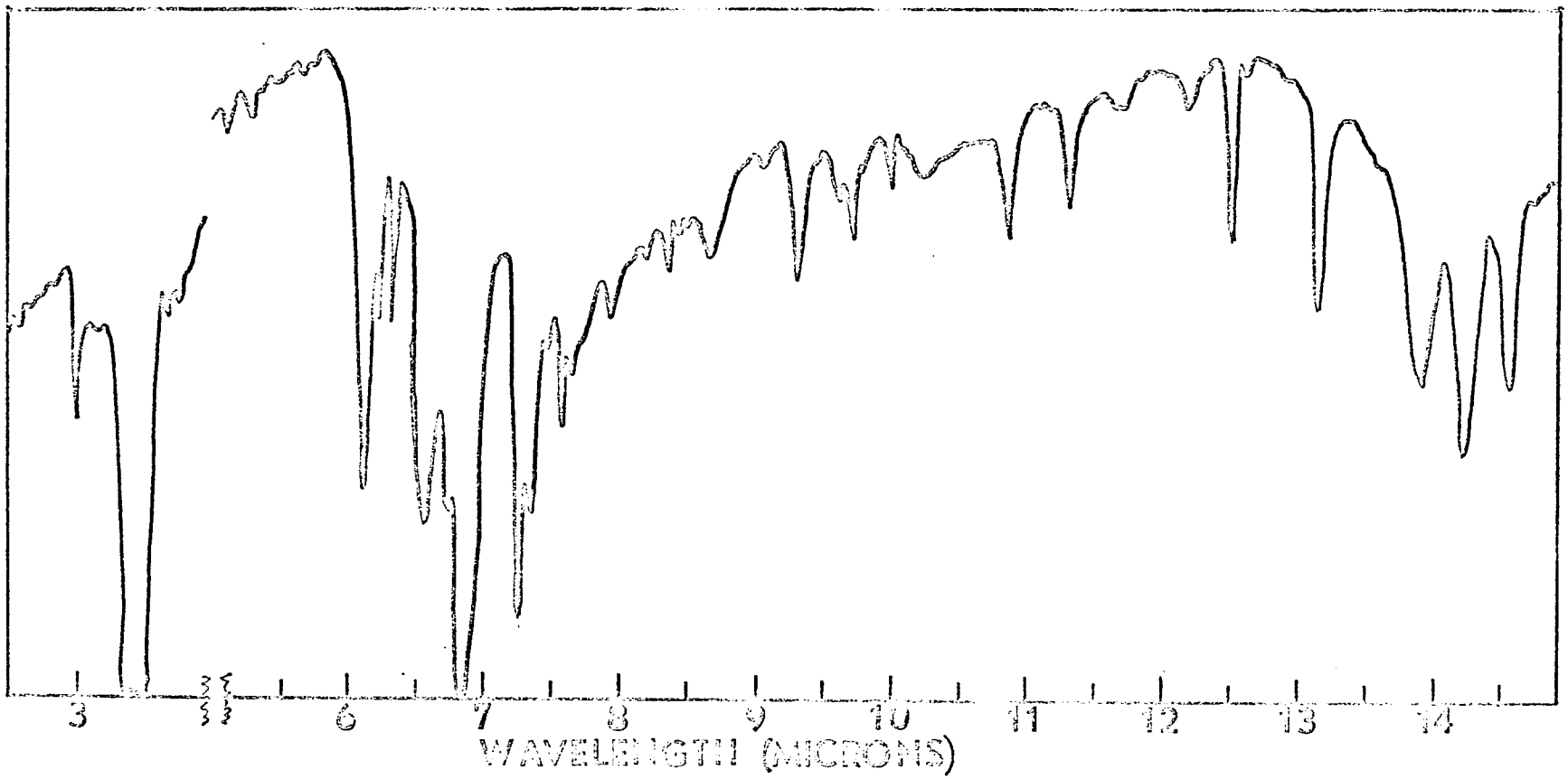

3
6
7
8
9
10
11
12
13
14
WAVELENGTH (MICRONS)

FIGURE 5

Infrared Spectrum (KBr) of

cis-N-(2-BENZAMIDOETHENYL)BENZAMIDE

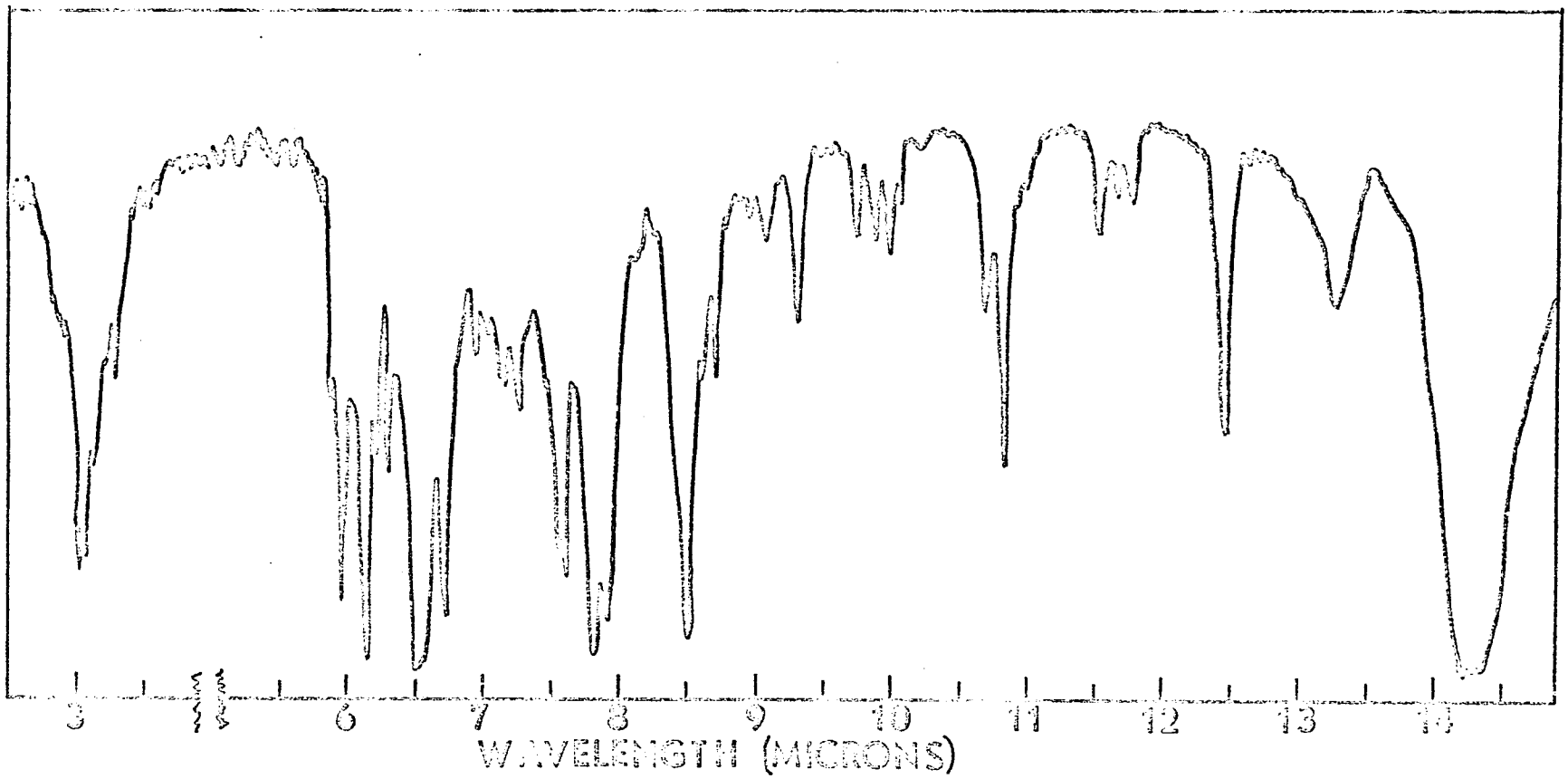

3
6
7
8
9
10
11
12
13
WAVELENGTH (MICRONS)

FIGURE 6

Infrared Spectrum (Nujol) of

trans-N-(2-BENZAMIDOETHENYL)BENZAMIDE

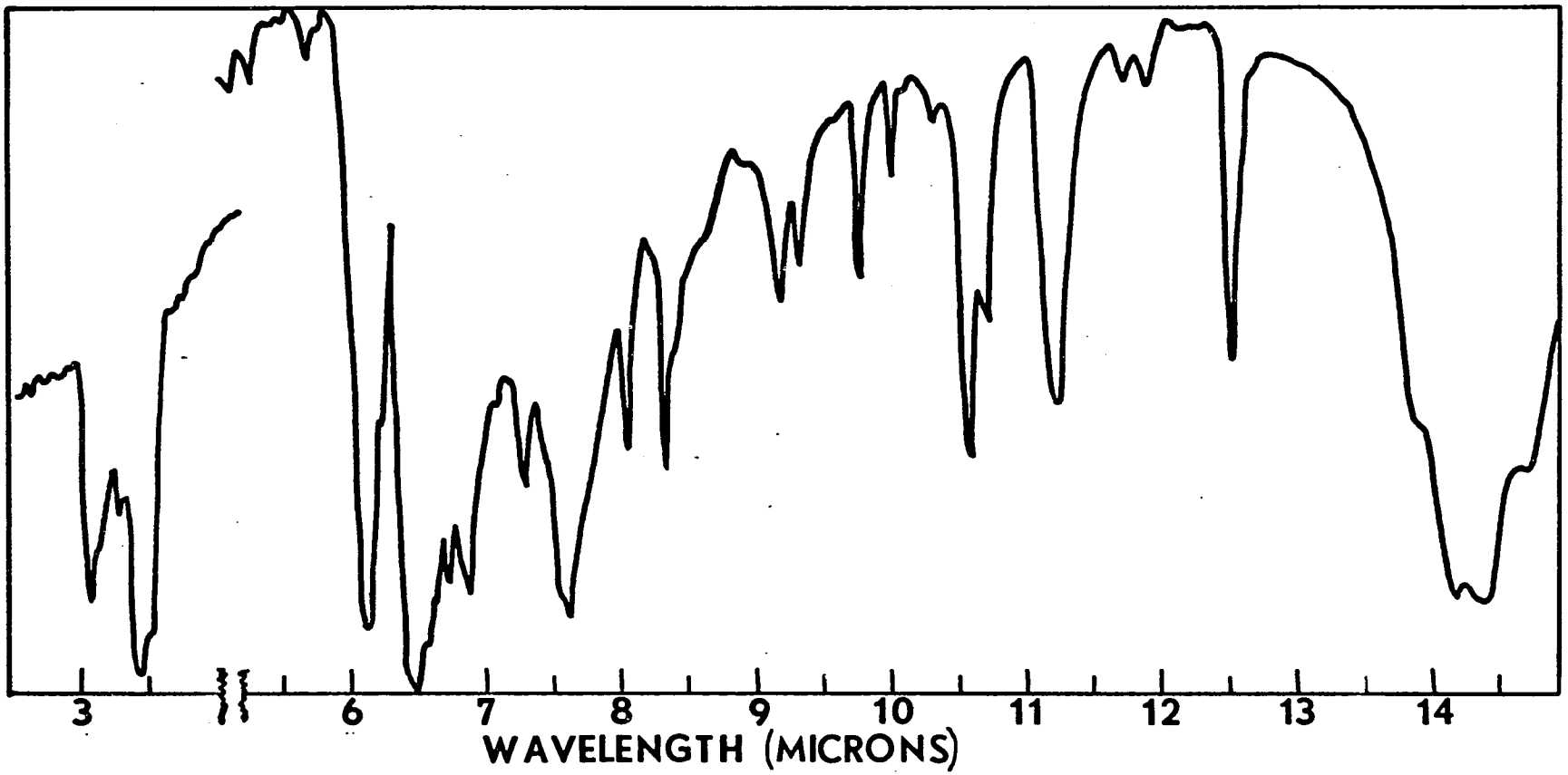

3
6
7
8
9
10
11
12
13
14
WAVELENGTH (MICRONS)

FIGURE 7

Infrared Spectrum (KBr) of

threo-N-(2-HYDROXY-1,2-DIPHENYLETHENYL)BENZAMIDE

(isolated from reaction mixture)

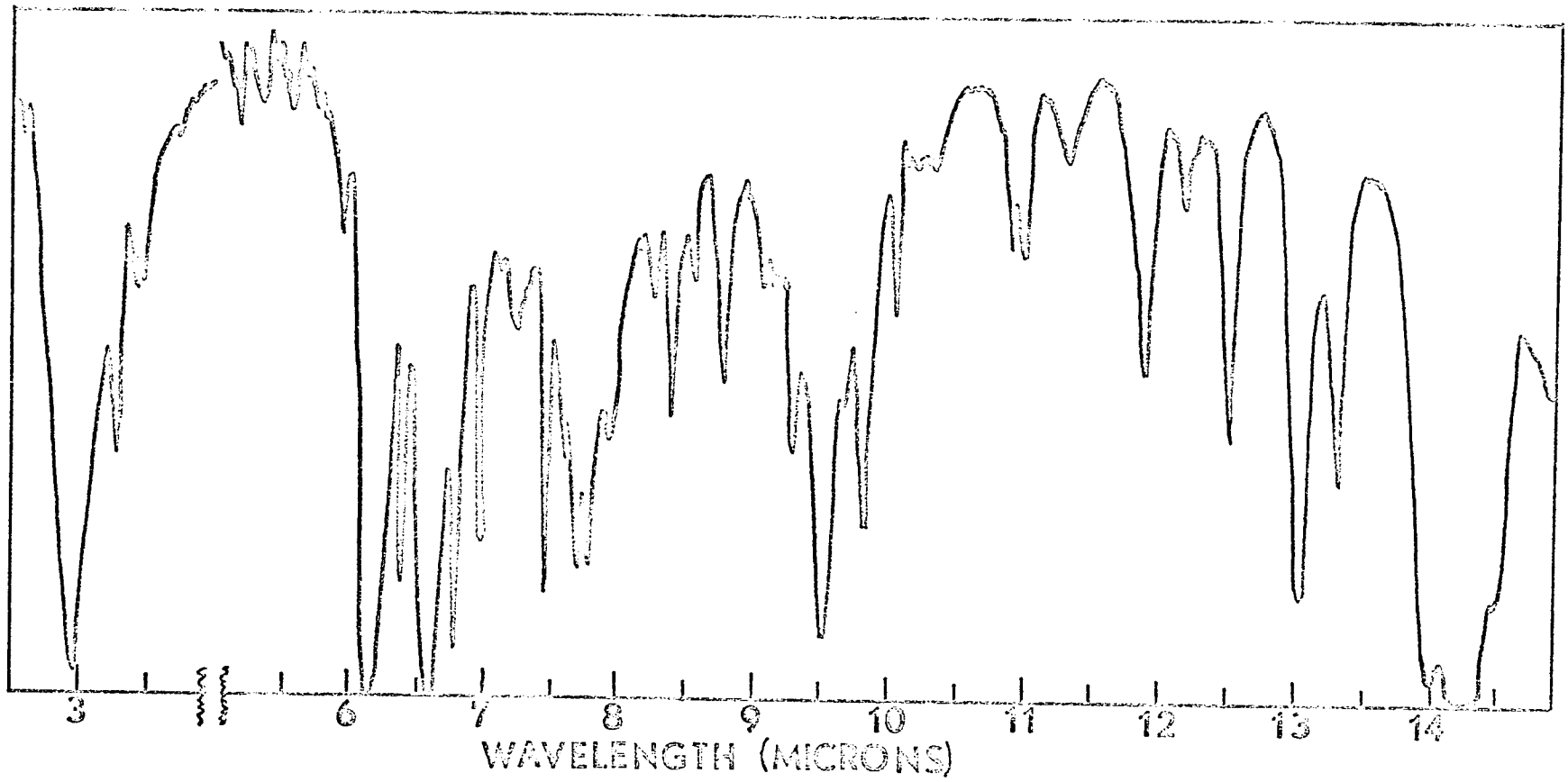

3
6
7
8
9
10
11
12
13
14
WAVELENGTH (MICRONS)

FIGURE 8

Infrared Spectrum (Nujol) of

threo-N-(2-HYDROXY-1,2-DIPHENYLETHENYL)BENZAMIDE

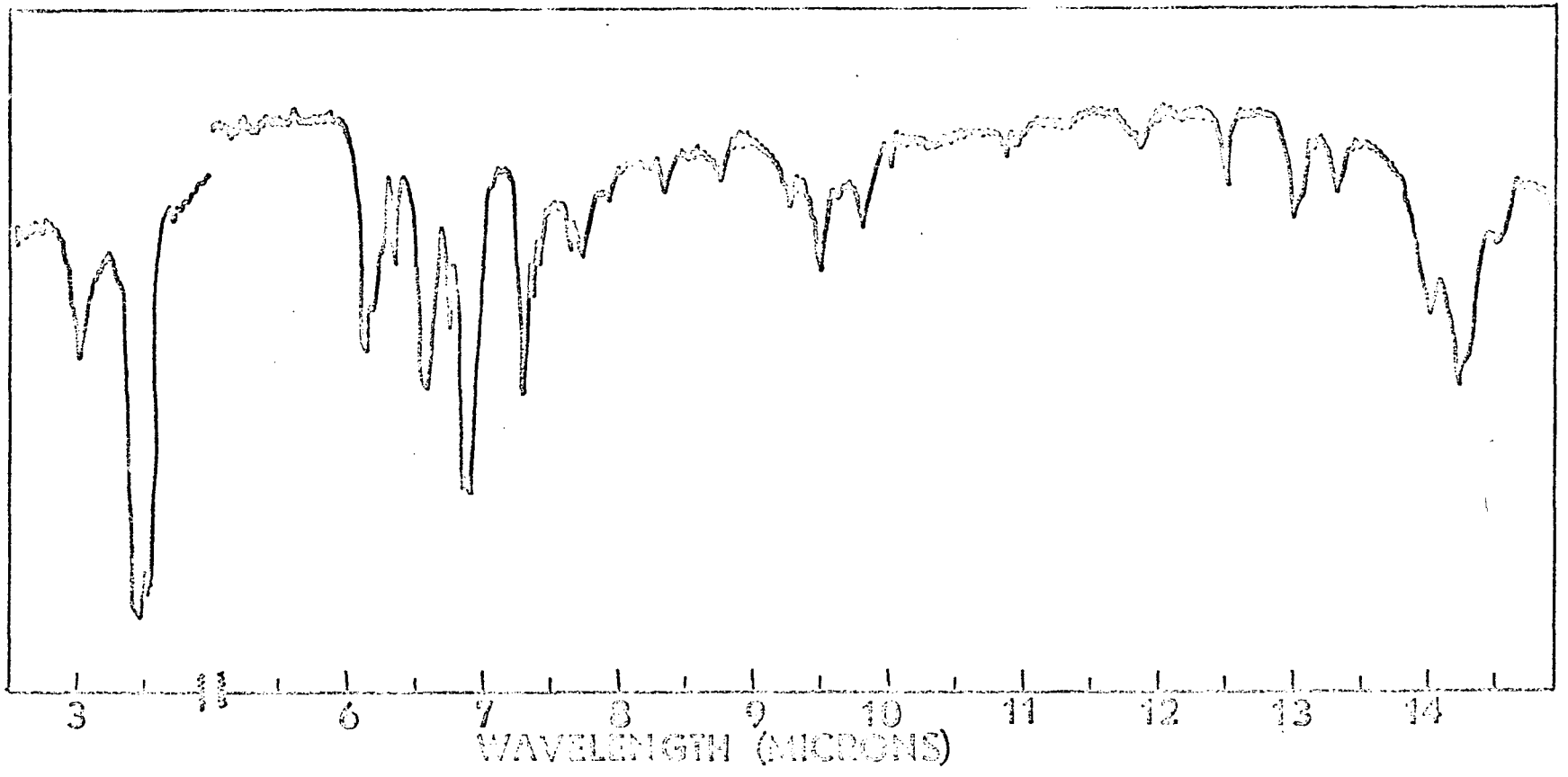
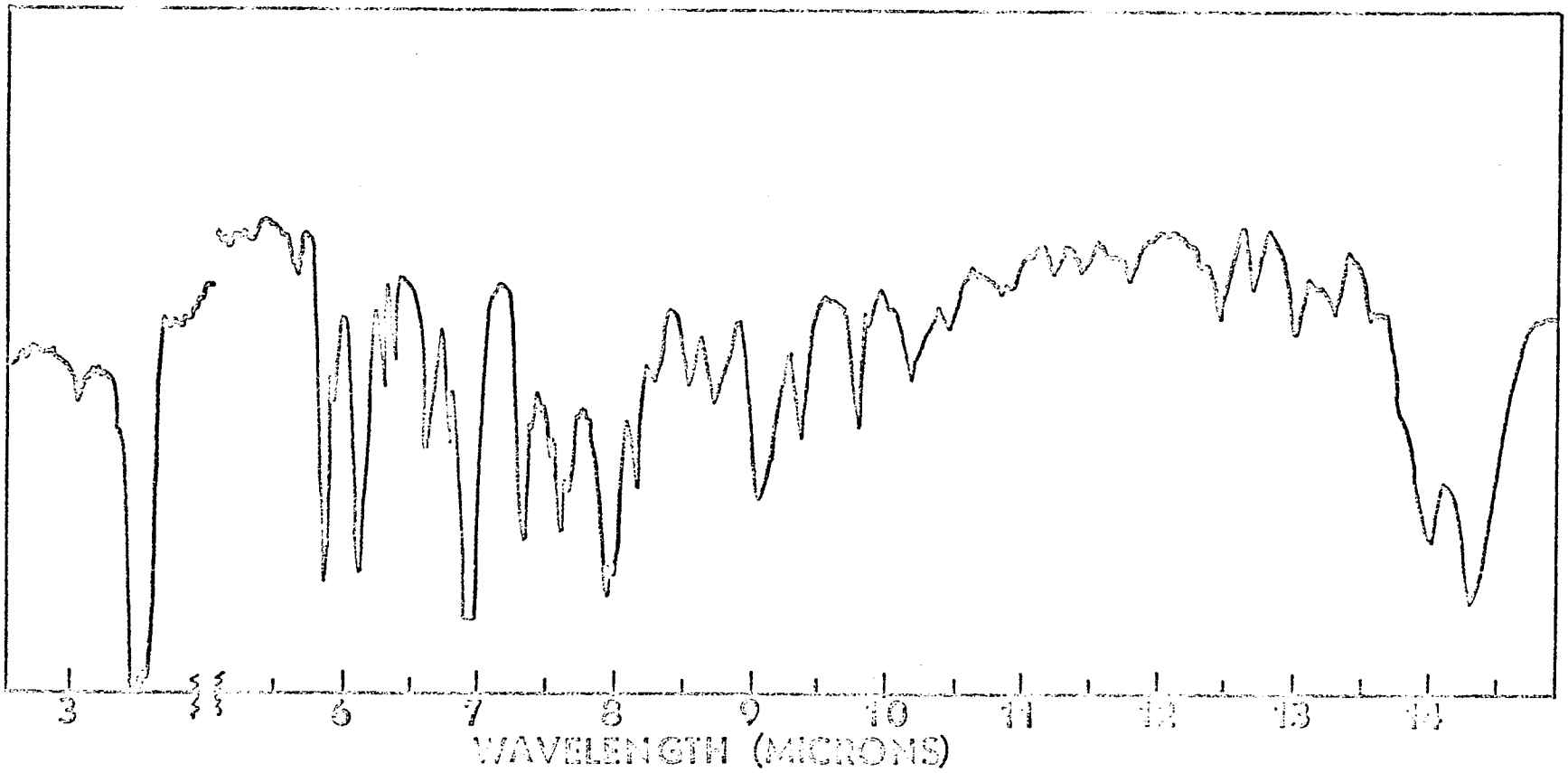

3
6
7
8
9
10
11
12
13
14
WAVELENGTH (MICRONS)

FIGURE 9

Infrared Spectrum (Nujol) of

N-(2-BENZOYLOXY-1,2-DIPHENYLETHYL)BENZAMIDE


3
5
7
8
9
10
11
12
13
14
WAVELENGTH (MICRONS)

APPENDIX C

Mass Spectra

FIGURE 10

Mass Spectrum of

cis-N-(2-BENZAMIDO-1,2-DIPHENYLETHENYL)BENZAMIDE

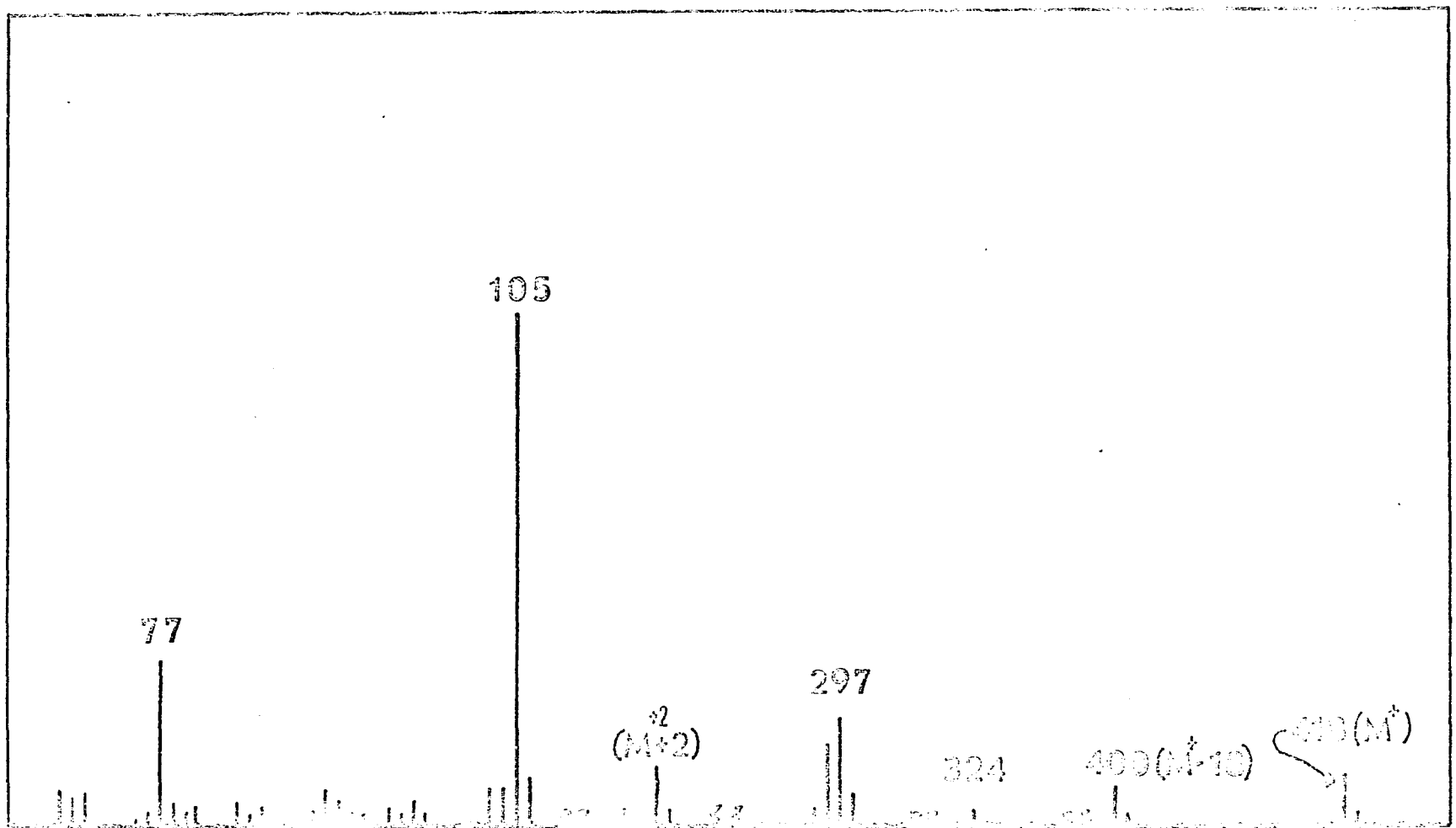

105
77
297
(M+2)
324
(M+)

FIGURE 11

Mass Spectrum of

cis-N-2-TOLUAMIDO-1,2-BIS-p-TOLYETHENYL)TOLUAMIDE

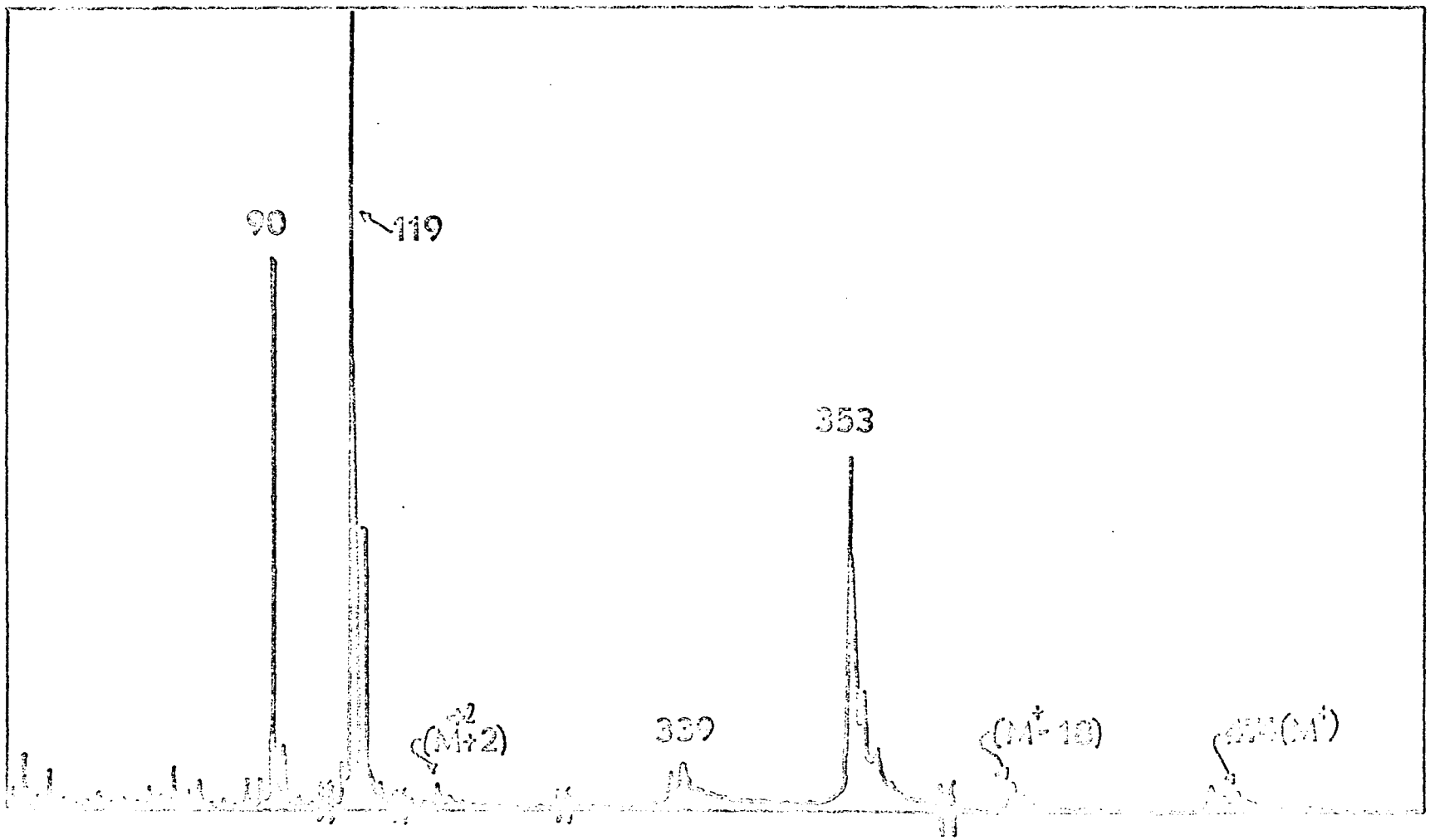

90
119
353
339
$(M^{+2})^{+2}$
$(M^{+}-19)$
(M^{+})

FIGURE 12

Mass Spectrum of

trans-N-(2-BENZAMIDOETHENYL)BENZAMIDE

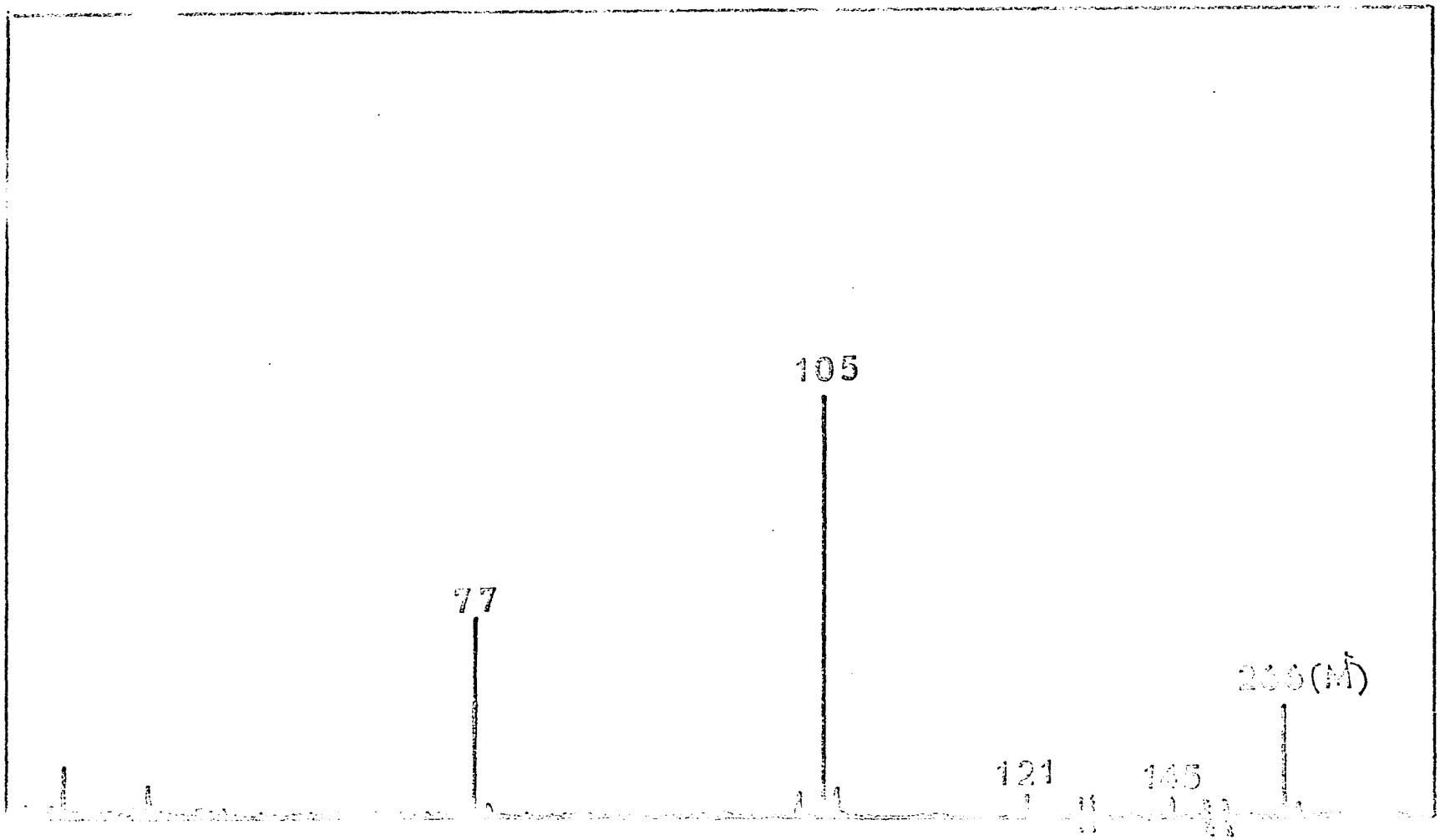

105
77
121
145

FIGURE 13

Mass Spectrum of

cis-N-(2-BENZAMIDOETHENYL)BENZAMIDE

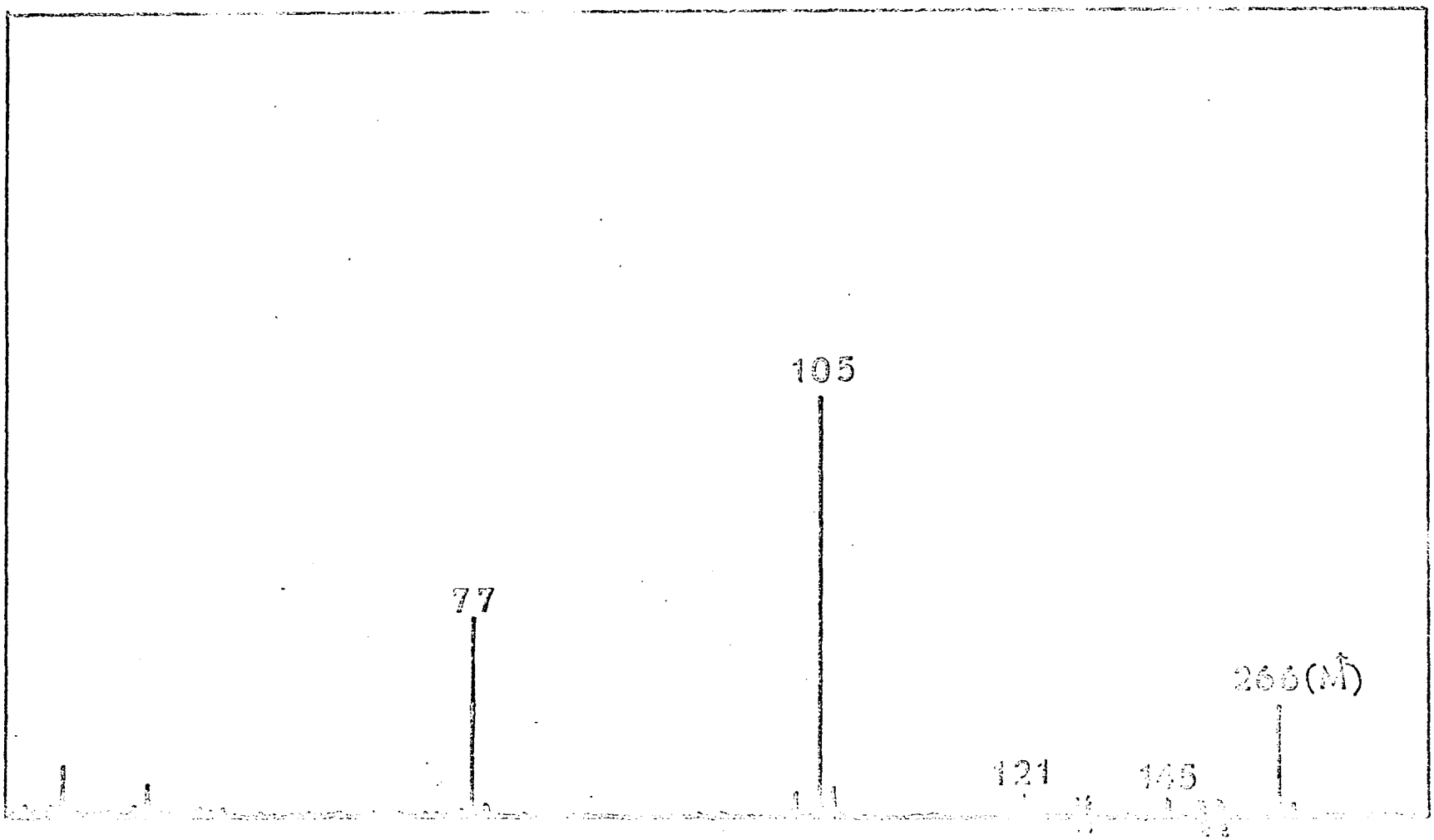

105
77
266(M)
121
145

FIGURE 14

Mass Spectrum of

threo-N-(2-HYDROXY-1,2-DIPHENYLETHENYL)BENZAMIDE

(isolated from reaction mixture)

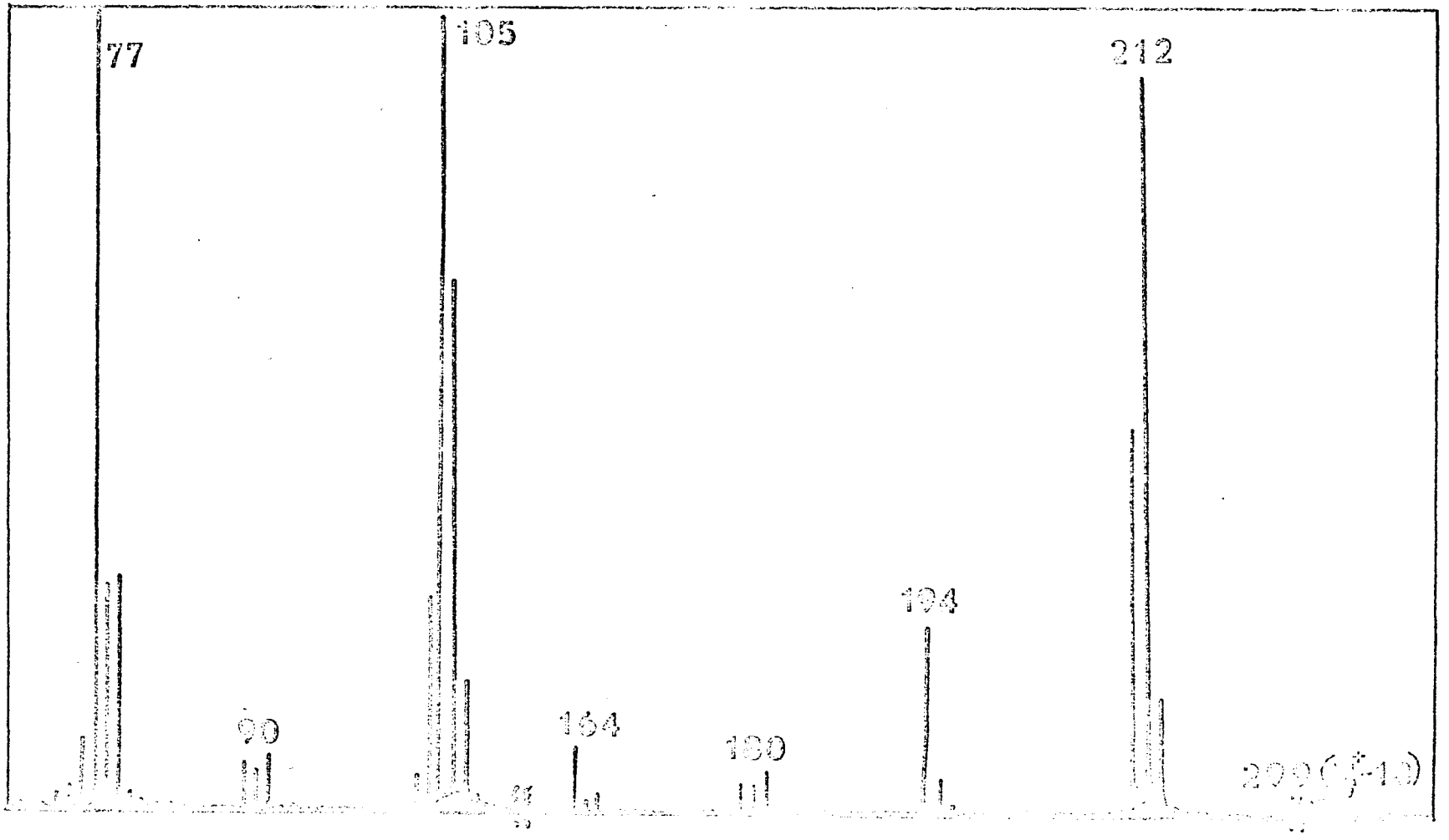

77
105
212
90
164
180
194
209(M-1)

FIGURE 15

Mass Spectrum of

threo-1,2-DIPHENYL-2-AMINOETHANOL

(from hydrolysis of Amide II)

FIGURE 16

Mass Spectrum of

threo-1,2-DIPHENYL-2-AMINOETHANOL

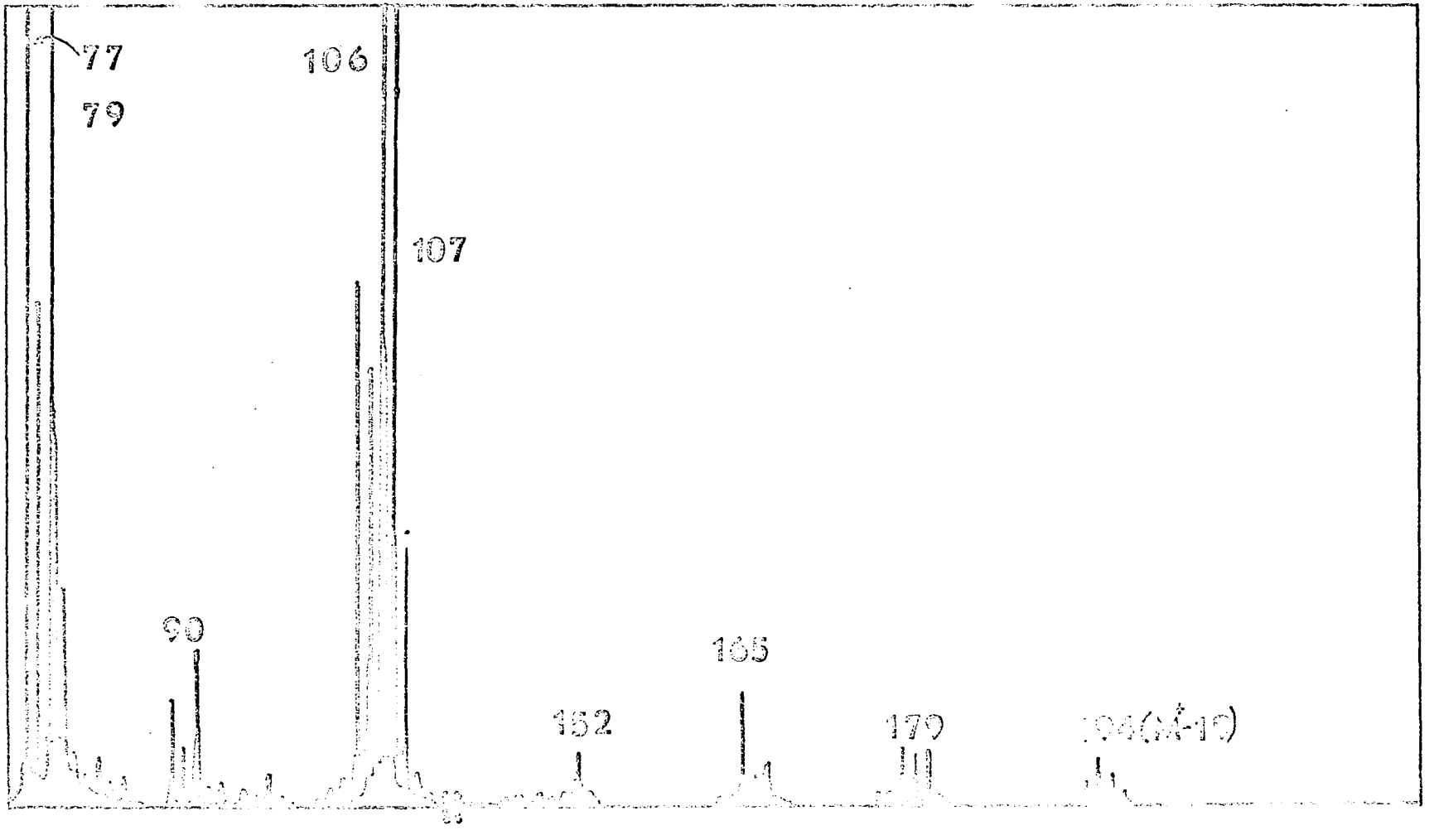

77
79
106
107
90
152
165
179
194(M-15)

FIGURE 17

Mass Spectrum of

erythro-1,2-DIPHENYL-2-AMINOETHANOL

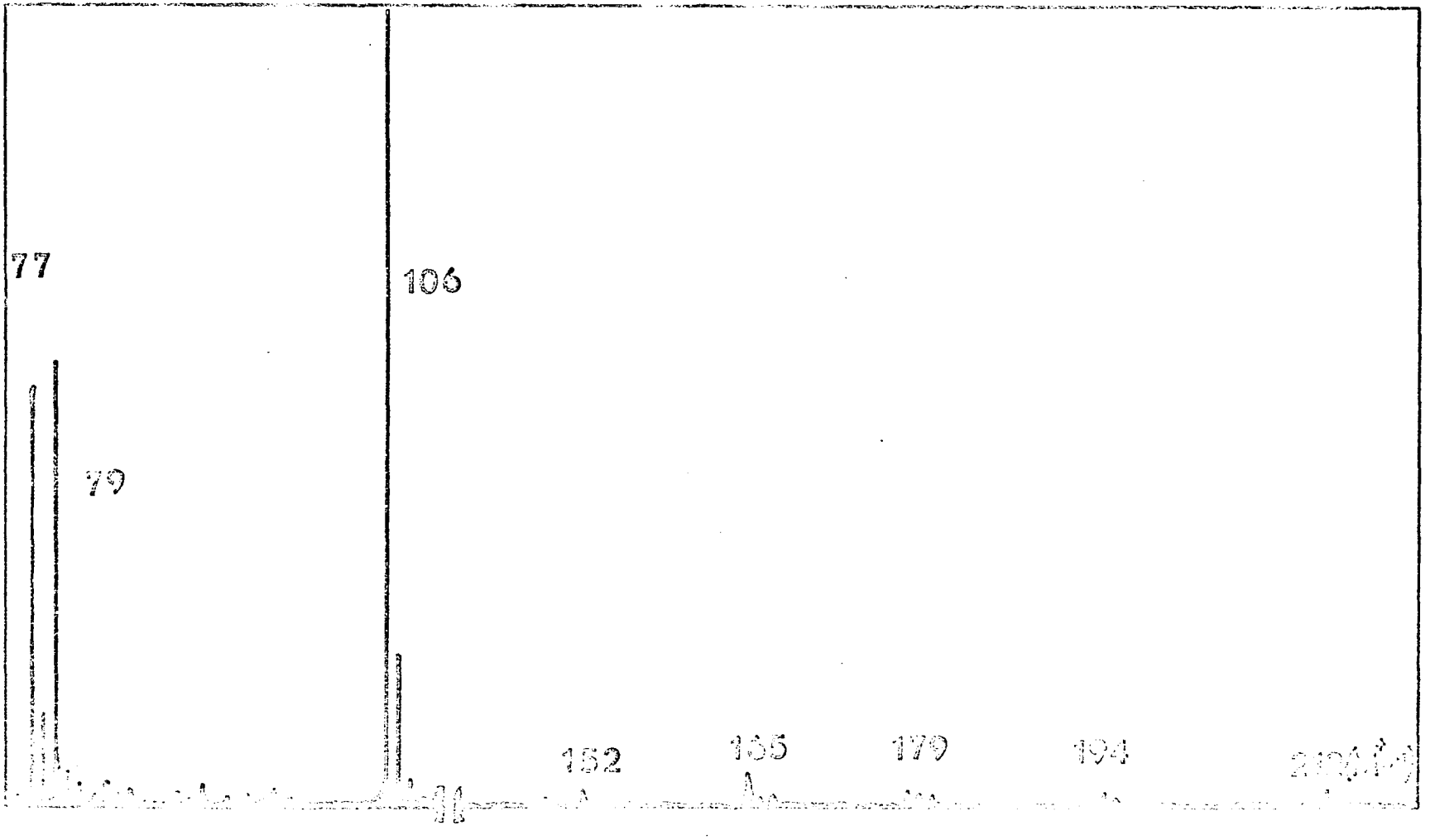
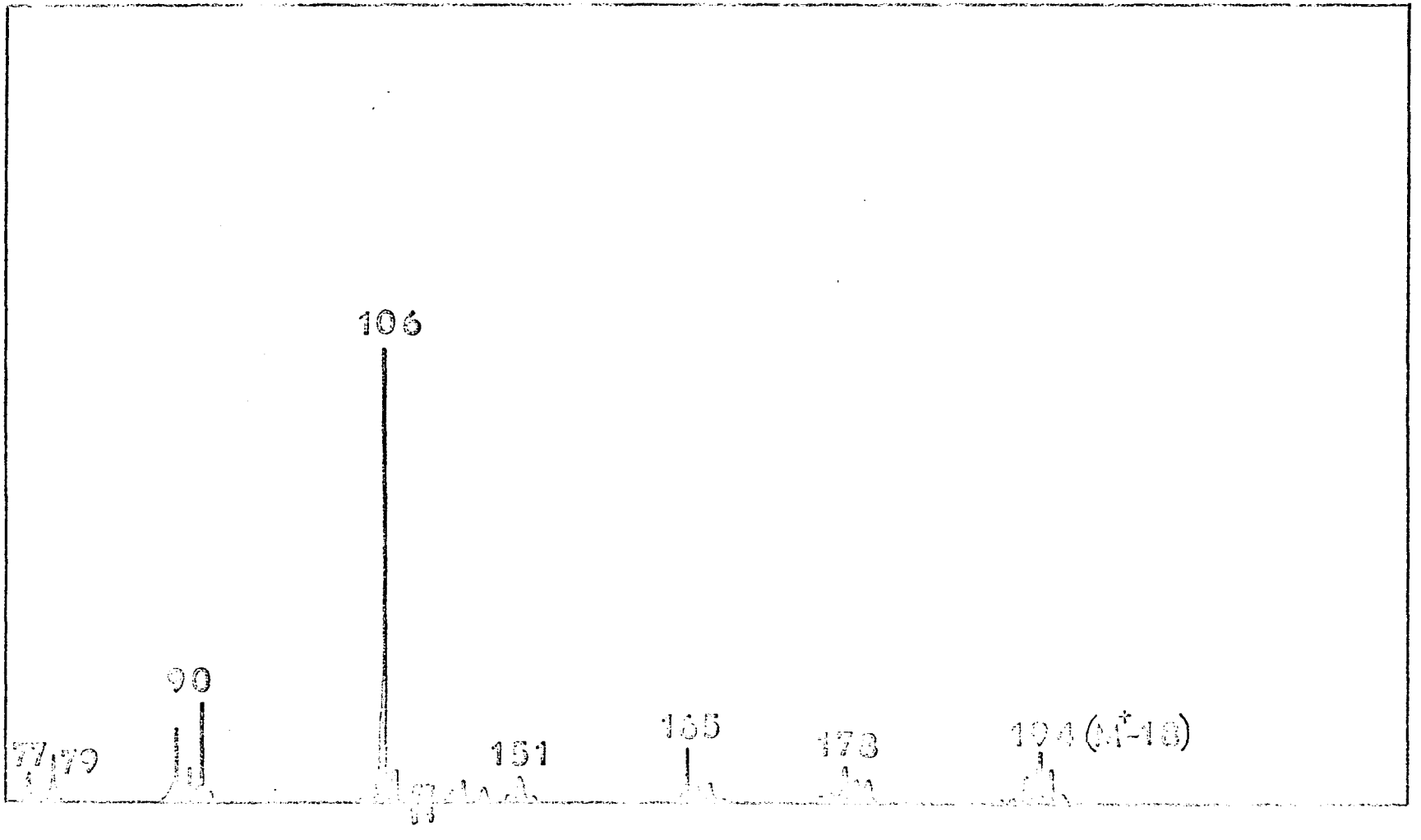

77
79
106
152
155
179
194

FIGURE 18

Mass Spectrum of

meso-1,2-DIPHENYLETHYLENEDIAMINE


106
90
77/79
151
165
173
194 (M+-15)

APPENDIX D

Nuclear Magnetic Resonance Spectra

FIGURE 19

Nuclear Magnetic Resonance Spectrum (DMSO-d_6) of

threo-N-(2-HYDROXY-1,2-DIPHENYLETHENYL)BENZAMIDE

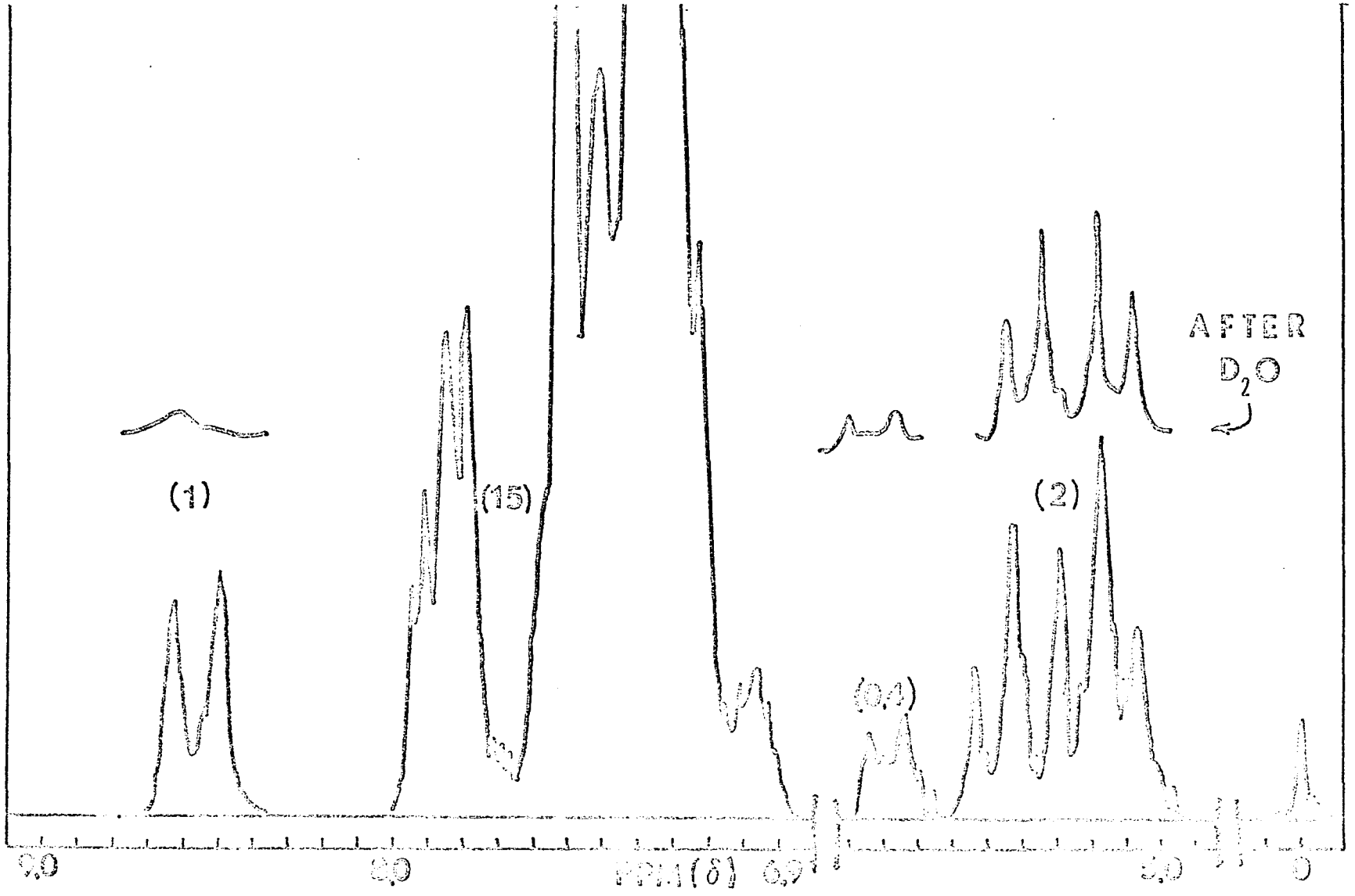

(1)
(15)
(0.1)
(2)
AFTER
D_2O
9.0
8.0
PPM (δ)
6.9
3.0
0

FIGURE 20

Nuclear Magnetic Resonance Spectrum ($CDCl_3$) of

threo-1,2-DIPHENYL-2-AMINOETHANOL

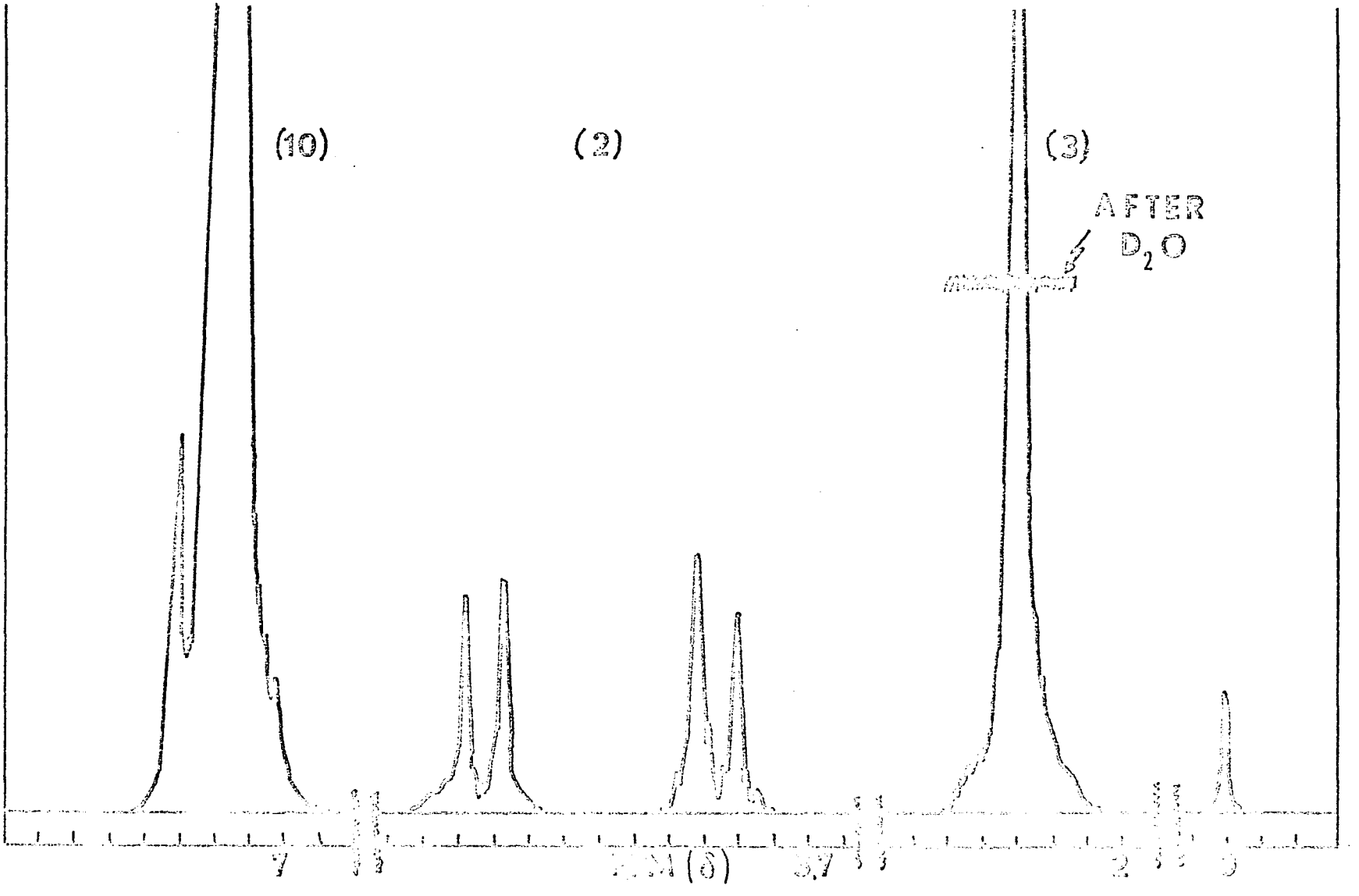
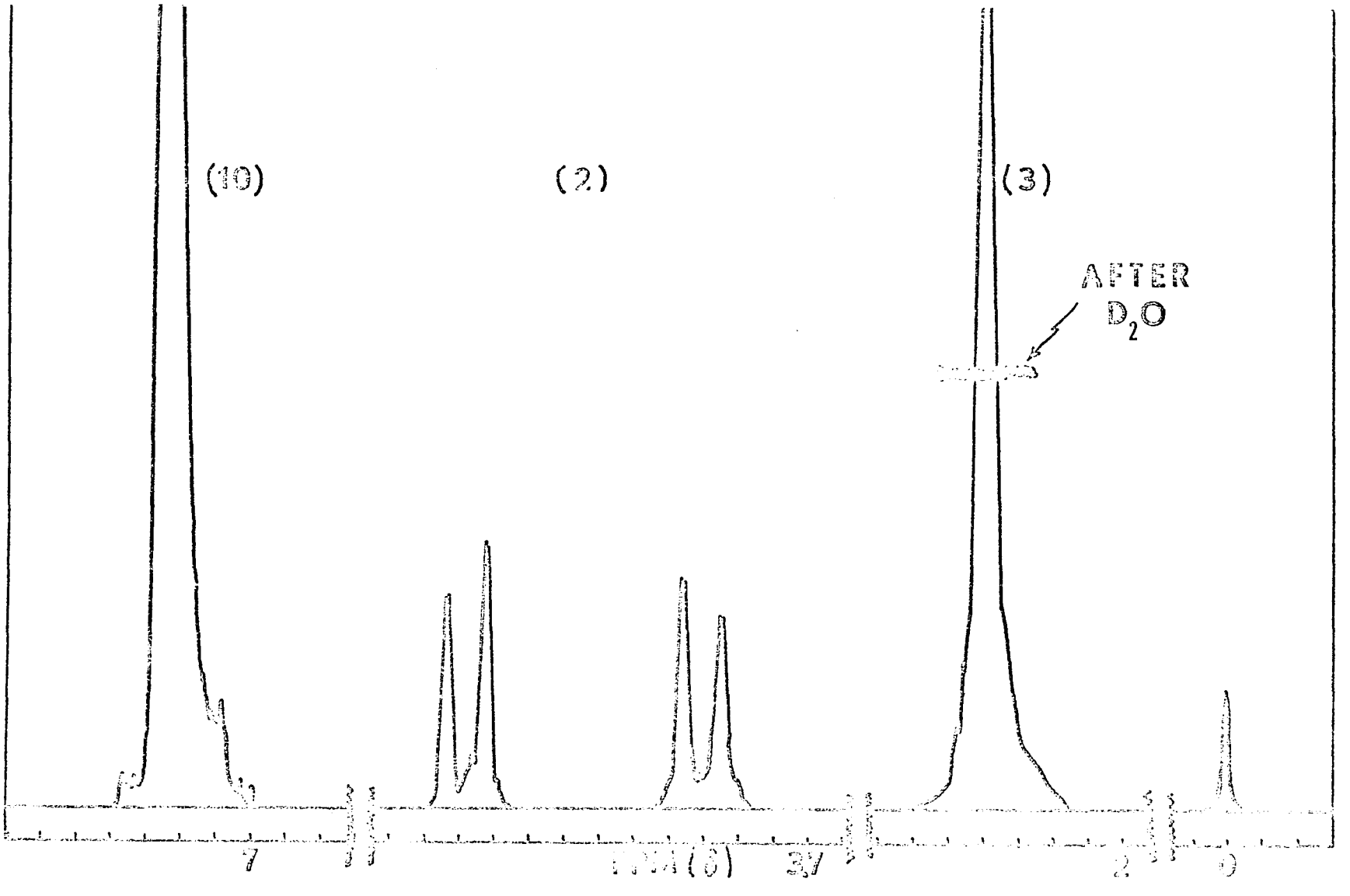

(10)
(2)
(3)
AFTER
D_2O
7
3.7
2
δ (PPM)

FIGURE 21

Nuclear Magnetic Resonance Spectrum ($CDCl_3$) of

threo-1,2-DIPHENYL-2-AMINOETHANOL

(from hydrolysis of Amide II)


(10)
(2)
(3)
AFTER
D_2O
7
3.7
2
δ

APPENDIX E

Reaction of Lithium Nitride with α-Chlorotoluene and Pyridine

Reaction of Lithium Nitride with Miscellaneous Organic Compounds.

α-Chlorotoluene.

A mixture of α-chlorotoluene (100 g., 0.80 mol.) and finely pulverized lithium nitride (1.6 g., 0.05 mol.) was stirred at reflux for 12 hrs. under nitrogen. A gradual change in color from red, characteristic of the dispersed nitride, to yellow was noted, along with the formation of a white flocculent solid. The inorganic solids were removed by filtration and tribenzylamine hydrochloride (8.0 g., 0.025 mol.) was precipitated from the filtrate by treatment with anhydrous hydrogen chloride. Treatment of the hydrochloride salt with excess aqueous sodium hydroxide gave the free amine, m.p. 87-90°. Recrystallization from aqueous ethanol afforded pure tribenzylamine (6.0 g., 0.0019 mol.), m.p. 92° (lit.[87] m.p. 92.5°) in 38% yield; infrared spectrum identical with Sadtler[23] spectrum No. 18,406.

Reaction of lithium nitride with ethyl iodide, n-butyl bromide, t-butyl bromide, n-hexyl bromide, chlorobenzene and iodobenzene was attempted; however, in all cases, only unreacted starting material was recovered.

Pyridine.

A mixture of pyridine (376 g., 4.7 mol.) and lithium nitride (22.5 g., 0.63 mol.) was stirred at reflux for 6 hrs. A gradual thickening of the mixture was noted along with an increase in pot temperature from 115 to 150°. A black solid (resinous mass) resulted on cooling. Treatment of this solid concurrently with water (200 ml.) and pyridine (25 ml.) on a steam bath for 1 hr., followed by filtration

afforded aqueous and organic phases. No tripyridylamine could be isolated from the aqueous layer. The organic layer was concentrated (187 g.) and vacuum distilled (1.2 mm) on a 15-inch Vigreaux column to yield four fractions:

Fraction No.	Temperature	Weight	Composition
1	103-106°	34 g.	Mixture of dipyridyls*
2	106-120°	22.1 g.	γ,γ'-dipyridyl†
3	120-145°	13 g.	γ,γ'-dipyridyl†
4	145-200°	15.2 g.	~ 10% γ,γ'-dipyridyl‡

*Column Chromatography.
†As determined by ir.
‡Mechanical separation of solidified γ,γ'-dipyridyl.

Crude γ,γ'-dipyridyl slowly solidified from all four fractions. Recrystallization from water gave pure γ,γ'-dipyridyl (41.3 g., 0.26 mol.) in 22% yield, m.p. 105-110° (lit.[88] m.p. 112°); infrared spectrum identical with Sadtler[23] spectrum number 2,026. α,α'- and α,γ'-Dipyridyls were isolated from the reaction mixture by chromatographing a 0.5 g. sample on Alcoa Alumina (F-20 grade, 30 g.) using benzene (100 ml.), benzene-chloroform (75:25, 100 ml.), benzene-chloroform (50:50, 150 ml.) and benzene-chloroform (25:27, 100 ml.) with collection of 25 ml. fractions. Fractions 1-5 were concentrated to yield pure α,α'-dipyridyl, while γ,γ'-dipyridyl was isolated from fractions 7-12 in 8 and 5% yields, respectively.

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VITA

Jules Michael Morris, son of Mr. and Mrs. Charles J. Morris, was born in New Orleans, Louisiana, on September 26, 1937. He attended St. Joseph Grammar School and graduated from Jesuit High School in 1955.

In the Fall of 1955, he entered Loyola University of the South in New Orleans, and in his senior year he served as president of the local chapter of the Student Affiliate of the American Chemical Society. In June, 1959, he received his B.S. in Chemistry. That fall, he entered the Graduate School of Louisiana State University in Baton Rouge, Louisiana, and accepted a graduate teaching assistantship in the Department of Chemistry. For the next four regular semesters he was an instructor in the organic laboratory course.

In August, 1961, he married the former Judith Ann Brock of New Orleans, Louisiana, and presently has three sons, Jules Jr., Brock, and Mark, and a daughter, Anne. After finishing the requirements for the Master of Science Degree, he was employed by Joseph Bancroft and Sons, Co., of Wilmington, Delaware, as a textile research chemist. In June, 1962, he returned to New Orleans and was employed by Chevron Chemical Company until September, 1966, when he re-entered Louisiana State University. For the next six regular semesters he was an instructor in Freshman Chemistry.

He is a member of Phi Lambda Upsilon, honorary chemical society, and is now a candidate for the Doctor of Philosophy Degree.

EXAMINATION AND THESIS REPORT

Candidate: Jules M. Morris

Major Field: Organic Chemistry

Title of Thesis: "Reaction of Lithium Nitride with Aromatic Aldehydes"

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

July 7, 1969